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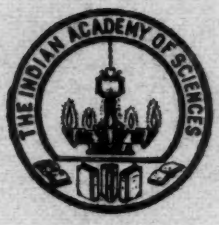

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THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

Part I. Raman Effect Data

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(*Memoir No.* 119 *from the Raman Research Institute, Bangalore-6*)

Received August 27, 1959

1. Introduction

A study of the Raman spectra of the hydroxides of the alkali and alkaline earth group of metals is inherently of interest in view of the simplicity of their chemical composition. There have been comparatively few investigations regarding them and the results reported refer only to the frequency shifts in the 3μ region. This paucity of data is attributable to the experimental difficulties of the subject; these substances are available only in the form of small crystals, polycrystalline masses or fine powders, and when the radiations of the mercury arc in the visible region are used for the excitation of the Raman spectra, the parasitic illumination entering the spectrograph is so strong as to obliterate any low-frequency shifts that might be observable in the vicinity of the exciting radiation. When the technique of exciting the Raman effect by the λ 2536·5 resonance radiation of mercury is employed, these difficulties are minimized and it becomes possible to record the low-frequency spectra at least in those cases where the material exhibits some measure of crystallinity and transparency. Since several of the hydroxides are also available as hydrates, it is of interest to study the Raman spectra of these hydrates as well. The first part of the present memoir deals with the facts of observation emerging from the experimental studies made with these substances.

Since the crystal structures of most of these substances have been determined already by X-ray diffraction methods and sometimes even through neutron-diffraction studies, the details of the spectra recorded are amenable to interpretation by the application of group theoretical methods and the second part of the memoir concerns itself with this. As all these substances crystallize in the holohedral class of their respective crystal systems, the rule of mutual exclusion is operative and hence the results of the Raman effect studies are complementary to those derived from infra-red studies and the latter do not therefore render the former superfluous.

The few infra-red investigations so far reported on these substances have all been restricted to the high-frequency region of 3μ to 15μ, evidently because of the experimental difficulties in the study of the far-infra-red region of the spectrum. That the present Raman effect data also afford a satisfactory explanation of the complex infra-red absorption spectra, reported in some cases in the 3μ region, will emerge in the third part of the memoir wherein we shall consider the infra-red data in relation to the Raman spectra of these substances.

2. EXPERIMENTAL TECHNIQUES

The spectra were recorded with a Hilger medium quartz spectrograph and in some cases with a Hilger Littrow spectrograph of higher resolving power. The general details regarding the experimental set-up and about the water-cooled magnet-controlled quartz mercury arc emitting the intense λ 2536·5 resonance radiation which was used for the excitation of the Raman effect have already been described in an earlier paper by the author (1957). It is pertinent to emphasize here that the results to be reported have been achieved chiefly because of the advantages inherent in the use of λ 2536·5 excitation, *viz.*, the intense scattering power in the ultra-violet region and the effective suppression by a filter of mercury vapour inside the spectrograph of the parasitic resonance radiation reaching the slit of the spectrograph, thereby enabling us to record the low-frequency spectrum clearly even in the cases of coarse crystals and polycrystalline masses. The large reactivity of these substances with the atmospheric moisture and carbon dioxide necessitated that they be sealed up in quartz tubes before recording their spectra.

With a slit width of 0·05 mm. exposures of the order of ten hours were found to be usually adequate to record the spectra with reasonable intensity and contrast. With increased exposures only the weaker mercury lines and the continuous background accompanying the spectrum of the mercury arc became prominent and any weak Raman lines recorded were masked by the general background intensity. Sometimes a few weak mercury lines appeared on the anti-Stokes side of the spectrum and care has been taken not to identify any of them as frequency shifts unless Raman lines of the same frequency shifts were present on the Stokes side as well. As a particular case of this, mention may be made of a group of lines noticed on the anti-Stokes side of the spectrum of $Ba(OH)_2 \cdot 8H_2O$, and which were not identified as Raman frequency shifts.

The following is a brief description of the several substances whose spectra were recorded in the present investigation:

(i) *Lithium hydroxide* (*anhydrous*).—The sample, made available through the kindness of a friend, was in the form of porous granules and exhibited no visible crystallinity. The sample actually contained a good proportion of $LiOH.H_2O$ as was revealed by the spectrum which exhibited the Raman lines due to pure $LiOH.H_2O$ also.

(ii) *Lithium hydroxide monohydrate*.—The material in the form of small lumps containing minute cyrstals was kindly provided by the Head of the Department of General Chemistry, Indian Institute of Science, Bangalore.

(iii) *Sodium hydroxide* (*anhydrous*).—The sodium hydroxide used in the study was the translucent polycrystalline mass commercially available in the form of sticks and manufactured by British Drug Houses, Ltd., and was of analytical reagent quality.

(iv) *Sodium hydroxide monohydrate*.—The monohydrated compound of NaOH was prepared by cooling a hot concentrated solution of the substance. The monohydrate is formed between 12·3° C. and 64·3° C. (Mellor, 1946).

(v) *Potassium hydroxide* (*anhydrous*).—In the case of KOH, the commercially available substance was found to be of the hydrated variety. Therefore, the pure substance (manufactured by the firm Merck & Co.) was heated in a nickel crucible in an attempt to drive out the water. The substance thus prepared was a white mass of fine texture. In spite of the heating, however, it was found that the spectrum continued to exhibit the hydroxyl frequency shift due to the hydrate by the side of that due to the anhydrous substance.

(vi) *Potassium hydroxide monohydrate*.—Near room temperature there are two hydrates of KOH, *viz*., the dihydrate and the monohydrate. The dihydrate is stated to melt at about 35° C. or slightly below and pass over into the monohydrate which is stable up to 143° C. (Mellor, 1946). The substance used in the present investigation was prepared by cooling a highly concentrated hot solution of KOH and the stability of this substance was checked up to 50° C. and was identified as the monohydrate.

(vii) *Calcium hydroxide*.—This is normally available only in the form of a fine powder. Crystals of this substance were grown by slowly evaporating a large volume of a saturated solution of $Ca(OH)_2$ at about 80° C. inside a thermostat. Owing to the very low solubility of the substance, the crystals obtained were quite small, being only a fraction of a millimetre in size. The material thus prepared contained a small proportion of calcium carbonate formed by the action of atmospheric carbon dioxide, as was revealed by the presence (faintly) of the principal frequency shift of the CO_3 group in the spectrum recorded.

(viii) *Magnesium hydroxide.*—The compound in the form of a colloidally fine powder was prepared by precipitation and was kindly made available by the Head of the Department of General Chemistry, Indian Institute of Science, Bangalore.

(ix) *Strontium hydroxide octahydrate.*—The substance in the form of small crystals, manufactured by Merck & Co., was used directly as such to record the spectra. The tetragonal crystal forms and the uniaxial nature of the crystal served to confirm their identification as the common octahydrate of $Sr(OH)_2$.

(x) *Barium hydroxide octahydrate.*—Small crystals of this substance (manufactured by Johnson & Sons) were used directly as such to record the spectra. That they were the common octahydrate of $Ba(OH)_2$ was confirmed by their biaxial nature and by the small optic axial angle exhibited by them (Winchell, *Microscopic Characters of Artificial Minerals*, pp. 187).

(xi) *Aluminium hydroxide.*—'Dry' aluminium hydroxide manufactured by British Drug Houses Ltd., in the form of fine powder, was used to obtain the spectra.

3. RESULTS

The frequency shifts observed in the case of the different substances are shown in Table I. The following are the principal features exhibited by the spectra of the several hydroxides. The observed frequency shifts group themselves and naturally fall into two specific regions, *viz.*, (*a*) a region of low-frequencies from about 75 cm.$^{-1}$ to 400 cm.$^{-1}$ and (*b*) a region between 3300 to 3700 cm.$^{-1}$ and which can readily be recognized as respectively the range of lattice frequencies and of hydroxyl frequencies. It is noteworthy that no frequency shifts have been observed in the region intermediate to the above ranges. The extremely fine texture and near opacity of some of the materials used in the study, *viz.*, LiOH, KOH, $Mg(OH)_2$ and $Al(OH)_3$, and the intense parasitic illumination consequent thereon reaching the slit of the spectrograph made it impossible to observe any low-frequency shifts in their cases. The spectra recorded have been grouped to form two Plates (II and III) and reproduce respectively the low and the high frequency regions.

In the majority of cases the high-frequency region exhibits only a single intense and sharp frequency shift contrary to our experience of the broad and diffuse bands observed with water and water of crystallization in the case of hydrated crystals. It is a surprising fact that in the cases of $LiOH \cdot H_2O$, $NaOH \cdot H_2O$ and $KOH \cdot H_2O$ the Raman bands due to water of crystallization

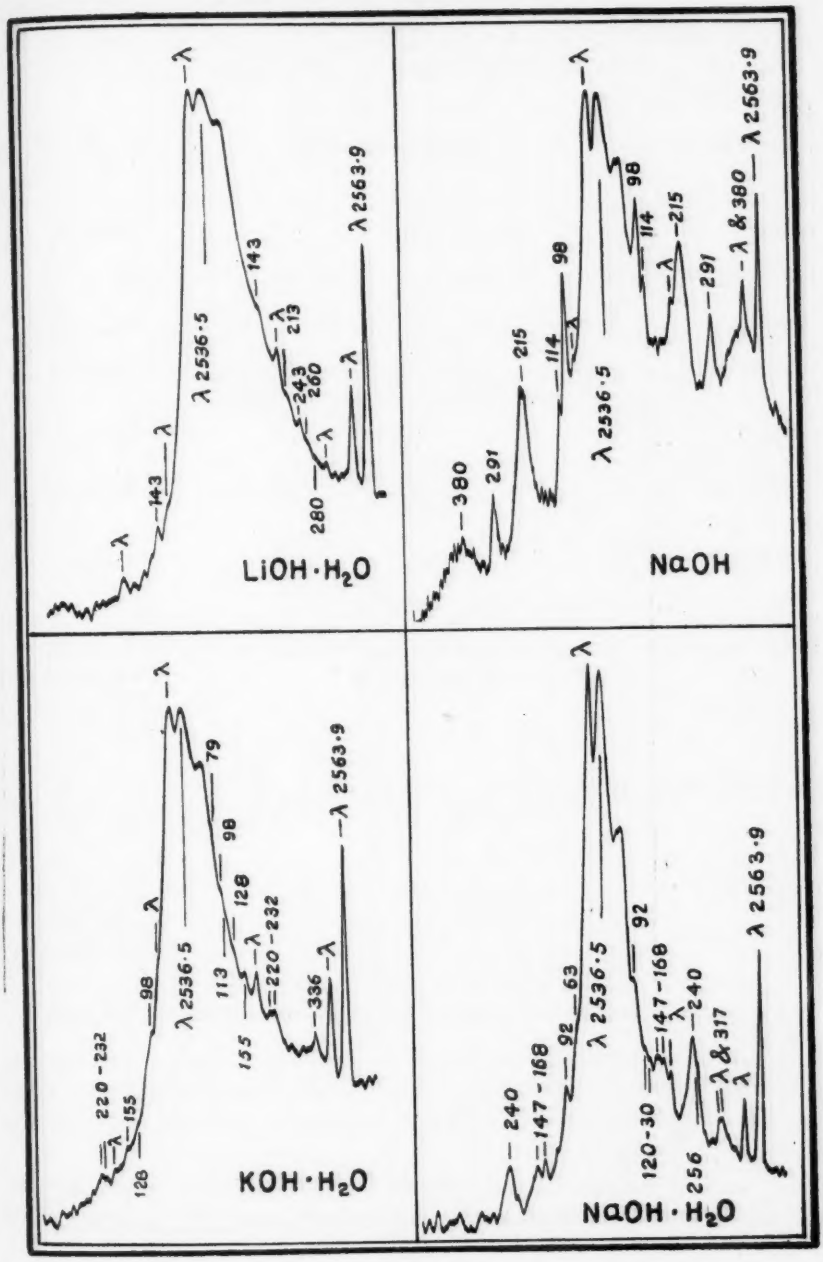

λ
143
λ
λ 2536·5
143
λ
213
243
260
λ
280
λ
λ 2563·9
LiOH·H2O
380
291
215
114
98
λ
λ 2536·5
98
114
λ
215
291
λ & 380
λ 2563·9
NaOH
220-232
λ
155
126
98
λ
λ 2536·5
79
98
128
113
λ
155
220-232
336
λ
λ 2563·9
KOH·H2O
240
147-168
92
63
λ 2536·5
92
120-30
147-168
λ
240
256
λ & 317
λ
λ 2563·9
NaOH·H2O

FIG. 1

TABLE I

Observed Raman frequency shifts in cm.$^{-1}$

Substance	Lattice frequencies	Internal frequencies
LiOH ..	..	3664 (*v.s.*)
$LiOH \cdot H_2O$ ..	143 (*s.*), 213 (*m.*), 243 (*m.*), 260 (*w.*), 280 (*w.*)	3563 (*v.s.*)
NaOH ..	98 (*v.s.*), 114 (*m.*), 215 (*v.s.*), 291 (*s.*), 380 (*w.b.*)	3632 (*v.s.*)
$NaOH \cdot H_2O$ ..	63 (*s.*), 92 (*s.*), 120 (*w.*), 130 (*w.*), 147 (*m.*), 168 (*m.*), 240 (*v.s.*), 256 (*w.*), 317 (*m.*)	3568 (*v.s.*)
KOH ..	..	3597 (*s.*)
$KOH \cdot H_2O$ ..	79 (*m.*), 98 (*s.*), 113 (*s.*), 128 (*s.*), 155 (*m.*), 220 (*m.*), 232 (*m.*), 336 (*m.*)	3501 (*v.s.*)
$Mg(OH)_2$ ..	..	3651 (*s.*)
$Ca(OH)_2$ ..	247 (*m.*), 282 (*m.*), 359 (*s.*)	3616 (*v.s.*)
$Sr(OH)_2 \cdot 8H_2O$	106 (*m.*), 132 (*s.*), 155 (*w.*), 173 (*m.*), 199 (*w.*), 230 (*v.s.*), 297 (*m.*), 328 (*w.*)	3302 (*m.b.*) 3393 (*m.b.*) 3488 (*v.s.*) 3536 (*w.*) 3593 (*w.*)
$Ba(OH)_2 \cdot 8H_2O$	106 (*s.*), 139 (*m.*), 156 (*m.*), 173 (*w.*), 205 (*v.s.*), 220 (*m.*), 276 (*m.*), 287 (*m.*), 328 (*w.*)	3335 (*w.b.*) 3481 (*v.s.*) 3529 (*s.*)
$Al(OH)_3$ ..	..	3369 (*s.*) 3431 (*m.*) 3521 (*s.*) 3583–3602 (*m.*)

s. = strong; *w.* = weak; *m.* = moderate intensity; *v.s.* = very strong; *b* = broad.

have not been recorded even though the hydroxyl frequency shift appears with large intensity. Even in the case of $Sr(OH)_2 \cdot 8H_2O$ and $Ba(OH)_2 \cdot 8H_2O$ the water bands appear only weakly in comparison with the large intensity of the shifts due to the hydroxide.

It may be noticed that the hydroxyl frequency shift (in anhydrous compounds) is generally higher in the case of substances with metallic ions of

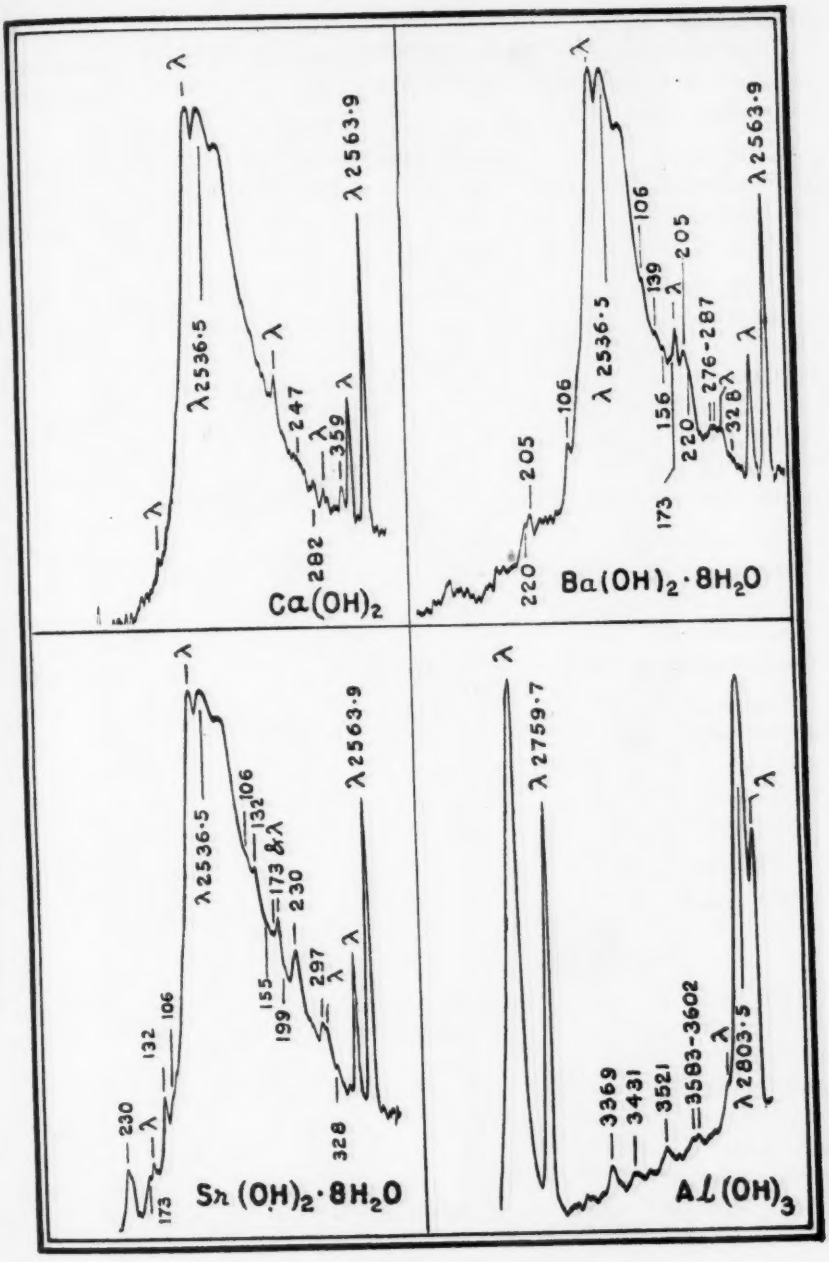

λ
λ 2536·5
λ 2563·9
247
359
282
Ca(OH)2
λ 2536·5
λ 2563·9
106
205
139
156
220
276-287
328
173
Ba(OH)2·8H2O
λ 2759·7
3369
3431
3521
3583-3602
λ 2803·5
Al(OH)3
λ 2536·5
λ 2563·9
106
132
173 & λ
230
155
199
297
328
230
132
106
173
Sr(OH)2·8H2O

FIG. 2

lower atomic weight. The hydroxyl frequency shifts in the cases of the hydrated hydroxides also form a similar sequence and are considerably lower (and less sharp) than the frequency shifts observed with the corresponding anhydrous compounds.

The lattice frequency shifts in the several cases exhibit diverse features with regard to their number, intensity and sharpness, all of which evidently have their origin in the differences in their crystal structures. To a discussion of these facts we shall return in the next part of the memoir.

The frequency shift of 282 cm.$^{-1}$ observed with $Ca(OH)_2$ coincides with the value of one of the lattice frequencies of calcite. The spectrum of the slightly impure $Ca(OH)_2$, as already mentioned, showed weakly the principal frequency 1086 cm.$^{-1}$ of calcite. However, the 282 cm.$^{-1}$ shift in calcite is relatively weaker than the 1086 cm.$^{-1}$ shift and it is highly improbable that the impurity of $CaCO_3$ was responsible for the 282 cm.$^{-1}$ shift. The identification of the shift as genuinely due to the $Ca(OH)_2$ is vindicated by the infra-red data as we shall see in Part III.

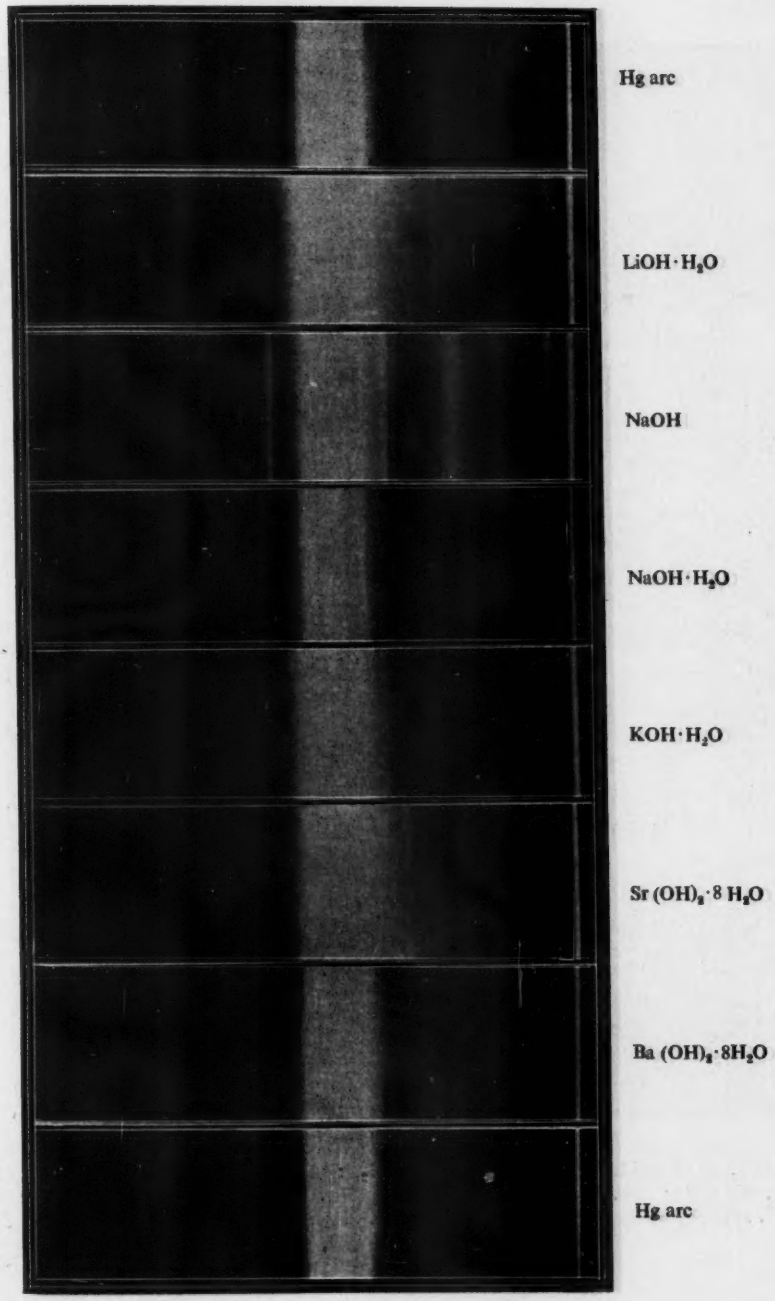
In order to exhibit several of the frequency shifts which were recorded rather faintly, microphotometer records of different cases (for the lattice frequency region) appear in the text. Figure 2 in the text includes also the microphotometer record of the spectrum of $Al(OH)_3$ in the hydroxyl frequency region since the spectrum recorded was too weak for reproduction.

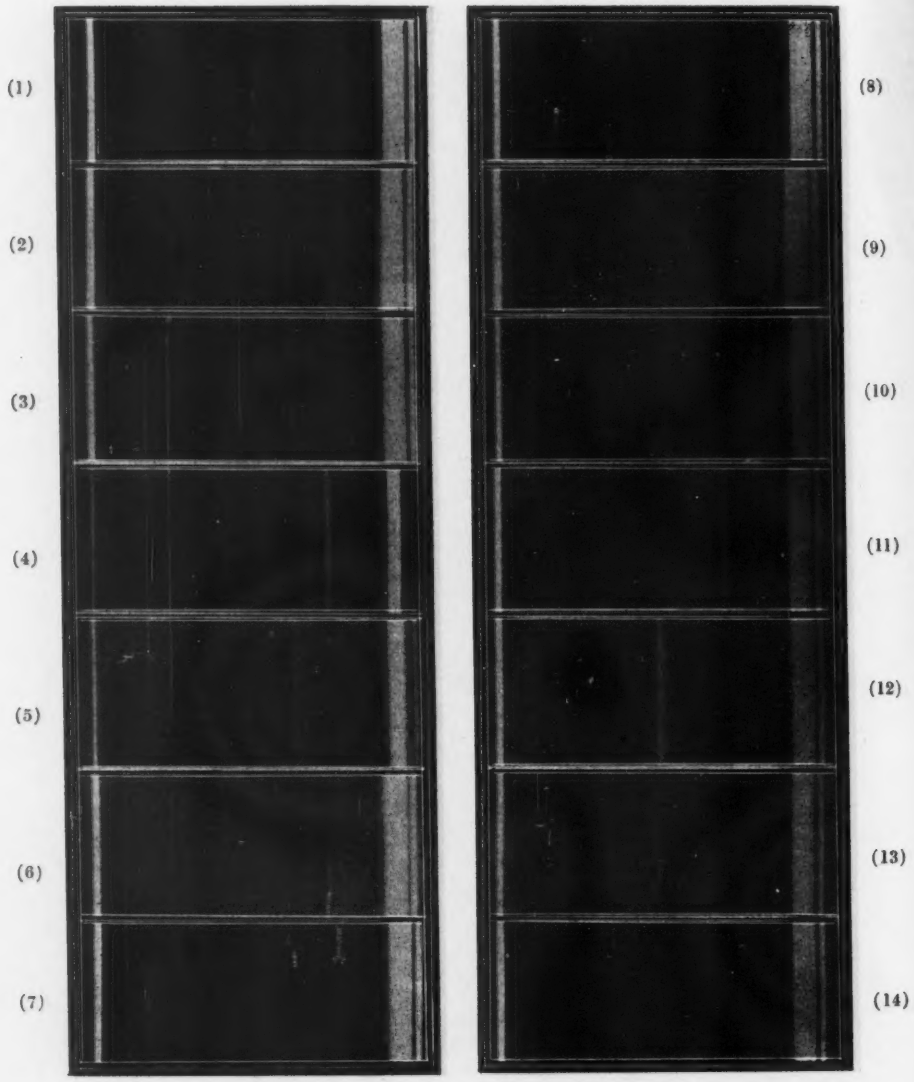
Some of the frequency shifts shown in Table I, *viz.*, 3632 cm.$^{-1}$ in the case of NaOH, and 3302, 3393 and 3488 cm.$^{-1}$ in the case of $Sr(OH)_2 \cdot 8H_2O$ and 3481 and 3529 cm.$^{-1}$ in the case of $Ba(OH)_2 \cdot 8H_2O$ have been reported by the earlier investigators, with minor differences in the observed values (Krishnamurti, 1930; Theimer, 1950; Busing, 1955).

The author wishes to express his sincere thanks to Professor Sir C. V. Raman, F.R.S., N.L., for his keen interest in this investigation.

4. SUMMARY

The paper reports the results of an investigation on the Raman spectra of eleven solid hydroxides using the λ 2536·5 resonance radiation of mercury arc for the excitation of the Raman effect. The cases studied (most of them for the first time) consist of the hydroxides of Li, Na and K and their monohydrates, the hydroxides of Ca, Mg and Al, and the octahydrated hydroxides of Sr and Ba. The facts of observation are discussed in relation to the crystal structure and the infra-red absorption data of these crystals in two separate parts following this paper.


Hg arc
LiOH·H2O
NaOH
NaOH·H2O
KOH·H2O
Sr (OH)2·8 H2O
Ba (OH)2·8H2O
Hg arc



FIGS. 1–14

Fig. 2. LiOH and $LiOH \cdot H_2O$; Fig. 3. $LiOH \cdot H_2O$; Fig. 4. NaOH; Fig. 5. $NaOH \cdot H_2O$; Fig. 6. $Mg(OH)_2$; Fig. 9. KOH and $KOH \cdot H_2O$; Fig. 10. $KOH \cdot H_2O$; Fig. 11. $Ca(OH)_2$; Fig. 12. $Sr(OH)_2 \cdot 8H_2O$; Fig. 13. $Ba(OH)_2 \cdot 8H_2O$. Figs. 1, 7, 8 and 14. Mercury spectrum.

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THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

Part II. Correlation with Crystal Structure

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1. Introduction

The application of conventional methods of group theory for elucidating the features observed in the Raman and infra-red spectra of crystals is well known and is dealt with in detail by Bhagavantam and Venkatarayudu in their treatise on the Theory of Groups. The group theoretical methods give the total number of vibrations appearing under each of the different symmetry classes and in addition it is usually possible to resolve this number into translatory, rotatory and internal vibrations. It had been pointed out by Bhagavantam[13] in his discussion of the case of crystalline Hg_2Cl_2 that in the case of crystals containing linear groups (like the hydroxyl ions figuring in our discussions) which possess only two degrees of rotational freedom, the usual formulæ used for resolving the total number of vibrations into the lattice and internal types of vibrations are inapplicable. However, since the symmetry properties and selection rules of the different irreducible representations of the various point groups have all been worked out and are readily available for reference (*vide e.g.*, *Molecular Vibrations* by Wilson *et al.*) it is possible from simple considerations of symmetry to picture the nature of the individual symmetry modes in simple cases. In the following we shall adopt this procedure of identification wherever feasible.

Crystal structure data naturally play an important role in the explanation of the observed facts. The relevant data are summarized in Table I. A list of references appears at the end of the paper and the numbers appearing in the first column of Table I refer to the concerned papers. In column 4 of the same table are shown the distances between the oxygens of the hydroxyl groups and in the case of the hydrates the figures marked with an asterisk denote the distances between the oxygens of the hydroxyls and the oxygens of the water molecules.

TABLE I

Details of crystal structure

Substance	Crystal system	Space group and number of units in primitive cell	O–O distance in A.U.	Characteristic features of the structure
LiOH[1] ..	Tetragonal	D^{7}_{4h} (2)	3·6	Layer structure normal to *c*. Each Li is surrounded by four hydroxyls nearly tetrahedrally. Each hydroxyl has four Li neighbours on one side and four hydroxyls of the next layer on the other side. Hydroxyls are parallel to *c*-axis. Site symmetry of Li: D_{2d}; of OH: C_{4v}.
$LiOH \cdot H_2O$[2]	Monoclinic	C^{3}_{2h} (2)	2·99 3·14 to 3.34*	Chain structure. Each Li surrounded nearly tetrahedrally by two hydroxyls and two water molecules. Site symmetry of oxygens of OH: σ_h; of Li: C_2; of O (H_2O): C_2.
NaOH[3–4] KOH[3]	Orthorhombic	D^{17}_{2h} (2) do.	3·40 3·26	Layer structure normal to *c*. Each Na is surrounded by five OH groups. OH ions are parallel to *c*. Na and O approximately in the *ab* plane. Characteristic double layers of Na and OH normal to *c*. Site symmetry for both Na and OH: C_{2v}. Similarly for KOH.
$NaOH \cdot H_2O$[5]	Orthorhombic	D^{15}_{2h} (8)	3·5 to 4·5 2·64 to 3·11*	Layer structure normal to *b*. No special positions of symmetry. Each Na surrounded by three hydroxyls and one H_2O nearly tetrahedrally. Each OH surrounded by 3 Na's and 2 H_2O's, and 3 OH's very much farther out than Na and H_2O.

TABLE I (*Contd.*)

Substance	Crystal system	Space group and number of units in primitive cell	O–O distance in A.U.	Characteristic features of the structure
$KOH \cdot H_2O$[6] ..	Monoclinic	C^5_{2h} (4)	2·63*	Layer structure parallel to (100). No special positions of symmetry. Oxygens (OH—OH_2—OH) form zigzag chains parallel to *c*.
$Mg(OH)_2$[7] ..	Trigonal	D^3_{3d} (1)	3·22	Layer structure normal to *c*. Hydroxyls parallel to *c*. Site symmetry of Mg: D_{3d}; of OH: C_{3v}. Each Mg is surrounded by six hydroxyls. Each OH is surrounded by three Mg's on one side and on the other side by three OH's of the next layer. Similarly for $Ca(OH)_2$.
$Ca(OH)_2$[8–9] ..	do.	do.	3·33	
$Sr(OH)_2 \cdot 8H_2O$[10]	Tetragonal	D^8_{4h} (4)	2·9 2·7*	Site symmetry of Sr: D_2; of oxygens of OH: C_4. The rest are in general positions. Each OH surrounded octahedrally by 4 H_2O's and 2 OH's.
$Ba(OH)_2 \cdot 8H_2O$[11]	Monoclinic	C^5_{2h} (4)		Atomic positions not determined. But all atoms are in general positions.
$Al(OH)_3$[12] ..	Monoclinic	C^5_{2h} (8)	2·75 to 3·46	All atoms in general positions. Distorted version of $Mg(OH)_2$ structure, the double layers of hydroxyls being parallel to (001). But only two-thirds of octahedral holes between hydroxyl layers are filled by Al. Owing to the distorted nature not all hydroxyls are parallel to *c* as in $Mg(OH)_2$.

* See text above for explanatory remarks.

2. The High Frequency Region of the Spectrum

The following facts regarding the crystal structures of the hydroxides enable us to readily account for the general features observed in the high frequency region of the spectrum. All the crystal structures shown in Table I belong to the centro-symmetric classes and the hydroxyl groups in the unit cell are separable into two halves related to each other by the centre of inversion. In many of the cases [*viz.*, LiOH, $LiOH \cdot H_2O$, NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$] the unit cell contains only two hydroxyl groups which are on either side of the centre of inversion. As a consequence there arise two coupled hydroxyl stretching vibrations which are respectively symmetric and antisymmetric with respect to the centre of inversion. In particular, in the cases of LiOH, NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$ where the hydroxyl groups occupy special positions of symmetry their symmetric vibrations actually belong to the totally symmetric class. In the case of $LiOH \cdot H_2O$ the positions of the hydrogens of the hydroxyls are not known. However, since it is remarked by Levy and Peterson[14] that the hydroxyl ion in $LiOH \cdot H_2O$ does not take part in hydrogen bonding, it appears highly probable that the hydrogens of the hydroxyls are situated on the symmetry plane, and the symmetric vibrations of the hydroxyls in this case also can easily be seen to belong to the class A_g of C_{2h}. The symmetric vibrations in all these cases are active only in the Raman effect. The vibrations appearing in the infra-red are antisymmetric and Raman inactive. The observation of a single frequency shift in each one of the above cases is hence in accordance with theory, and these shifts are identified with the internal vibrations of the hydroxyls belonging to the totally symmetric class.

With regard to substances which contain more units in the primitive cell, the coupled internal vibrations of the hydroxyls can be divided into two groups of equal number of vibrations which are characterized by the fact of their being symmetric or antisymmetric with respect to the centre of inversion. With the exception of $Sr(OH)_2 \cdot 8H_2O$, in all the remaining cases wherein the atoms are situated in general positions, *i.e.*, in the case of $NaOH \cdot H_2O$, $KOH \cdot H_2O$, $Ba(OH)_2 \cdot 8H_2O$ and $Al(OH)_3$, all vibrations which are symmetric with respect to the centre of inversion are Raman active. Hence, the spectra of $NaOH \cdot H_2O$, $KOH \cdot H_2O$, $Ba(OH)_2 \cdot 8H_2O$ and $Al(OH)_3$ should according to theory exhibit respectively 4, 2, 4 and 12 components due to the internal vibrations of the hydroxyls. However, it is obvious that only the modes in which the internal vibrations of all the hydroxyls take place in identical phase (*i.e.*, totally symmetric class) would be intensely Raman active, the others being relatively weak. Also, if the hydroxyl groups are far removed from each other as in $NaOH \cdot H_2O$ the coupling between the

hydroxyls will be too weak for the differences in the phases of adjacent groups to influence the frequency shift observably. In particular, in $NaOH.H_2O$ the eight units of the primitive cell are distributed equally in two adjacent layers which are quite far apart, the spacing being 5·9 A.U. In these circumstances, the appearance, in the spectra, of fewer components than that predicted by theory may be ascribed to either the low intensity of some of the components and (or) to their falling too close to the totally symmetric frequency to be resolved from it.

In view of the foregoing remarks the frequency shifts observed at 3568 cm.$^{-1}$ in $NaOH.H_2O$ and at 3501 in $KOH.H_2O$ may be assigned to the totally symmetric class. The appearance of two strong components well separated from each other at 3481 and 3529 cm.$^{-1}$ in the case of $Ba(OH)_2.8H_2O$ is indicative of considerable coupling between the hydroxyls of the unit cell; the former which is more intense evidently belongs to the totally symmetric class. In the case of $Al(OH)_3$ five components, some of them rather broad, have been observed at 3369, 3431, 3521, 3583 and 3602 cm.$^{-1}$ It is probable that some of them are unresolved groups of lines. The distribution of the observed frequencies over a considerable range is due to the large differences in the distances between the several hydroxyls in the unit cell and correspondingly varying degrees of interactions between them.

In the case of $Sr(OH)_2.8H_2O$ since there are eight hydroxyls per unit cell, there are, in all, four coupled internal vibrations symmetric with respect to the centre of inversion. Unlike the cases discussed above, the group D_{4h} to which $Sr(OH)_2.8H_2O$ belongs contains an irreducible representation A_{2g} symmetric with respect to the centre of inversion and which is Raman inactive. Since the positions of the hydrogen atoms are not known, it is not possible to determine the exact number of components active in the Raman effect. Three components have been observed at 3488, 3536 and 3593 cm.$^{-1}$; the intense line at 3488 cm.$^{-1}$ most probably belongs to the totally symmetric class.

In the case of hydrated hydroxides, the spectrum should in addition exhibit frequency shifts due to the water molecules. According to theory the Raman spectrum of water vapour should exhibit three frequency shifts. Only a single strong frequency shift (of the symmetric class) at 3655 cm.$^{-1}$ had been so far observed, the two other vibrations being presumably too weak (*vide Infra-red and Raman Spectra* by Herzberg). However, they have been observed in the infra-red spectrum at 1595 and 3756 cm.$^{-1}$ Considerations similar to that put forward for the explanation of the hydroxyl

frequencies indicate that corresponding to the 3655 cm.$^{-1}$ shift of water vapour, the spectra of $LiOH \cdot H_2O$, $NaOH \cdot H_2O$, $KOH \cdot H_2O$ and $Ba(OH)_2 \cdot 8\,H_2O$ should exhibit respectively 1, 4, 2 and 16 components which arise due to the coupling of the vibrations and which take place symmetrically with respect to the centre of inversion. In the case of $Sr(OH)_2 \cdot 8\,H_2O$, 16 components are possible. But, the actual number that should be expected to appear in Raman effect cannot be determined in the absence of any data regarding the positions of the hydrogens. The fact that no shifts due to water are observed with $LiOH \cdot H_2O$, $NaOH \cdot H_2O$ and $KOH \cdot H_2O$ is rather surprising and it requires further experimental study with clear and large crystals to observe them. The broad bands at 3302 and 3393 in $Sr(OH)_2 \cdot 8\,H_2O$ and 3335 cm.$^{-1}$ in $Ba(OH)_2 \cdot 8\,H_2O$ are evidently due to the large number of shifts appearing unresolved from each other. The explanation of the diminution of these frequencies from the value of 3655 cm.$^{-1}$ for water vapour, we shall consider in the following section.

3. Hydroxyl Bonding Effects

The large variations in the hydroxyl frequency shifts observed in the different cases are explicable as arising due to the interactions between the different hydroxyls (and the water molecules as well in the hydrates) which are contiguous to each other. Bernal and Megaw[15] have discussed in detail the nature of the interactions between hydroxyl groups—called by them the hydroxyl bond to distinguish it from the hydrogen bond. In the case of interactions between hydroxyl groups the distances between the groups are comparatively large (ranging from 2·75 to 3·6 A.U.). (In the case of hydrogen bonding, the oxygen atoms approach to within 2·55 A.U. of each other and the hydrogen linking them is not preferentially attached to either of them.)

The studies on the structure of $Al(OH)_3$ and other hydroxides have led Bernal and Megaw (*loc. cit.*) to conclude that there exists an attractive force between the hydroxyls. The hydroxyl ion can be pictured to be made up of an O^{--} and a proton H^{+} and as a result the negative charge of one oxygen can attract the positive charge of a neighbouring hydrogen to form the hydroxyl bond. It follows that the attraction will be greater at shorter O–O distances and will result in the displacement of the hydrogen atom from its normal position near the oxygen to which it belongs and as a consequence a diminution of the hydroxyl frequency would result. However, this is only a simplified picture of the actual state of affairs and, in general, the effects of all the surrounding neighbours will have to be taken into account. Especially in cases like LiOH, NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$ where the hydroxyl groups are far apart and are orientated parallel to each other and normal to

the layers, no large diminution of the frequency can be expected to occur. Even so, the fact that the hydroxyl frequency shifts in LiOH, NaOH and KOH (3664, 3632 and 3597 cm.$^{-1}$) follow the same sequence as the O–O distances in them (3·6, 3·4 and 3·26 A. U.) is significant. In the case of Ca $(OH)_2$ and Mg $(OH)_2$ the O—O distances are respectively 3·33 and 3·22 A.U. Their respective hydroxyl shifts 3616 and 3651 cm.$^{-1}$ fall in the region approximately near that of NaOH; however, it is surprising that the frequency shift in Mg $(OH)_2$ should be higher than that in the case of Ca $(OH)_2$.

In the case of the hydrates additional interactions arise between the hydroxyl ions and the water molecules contiguous to them. The progressive diminution of the frequency shifts in $LiOH \cdot H_2O$, $NaOH \cdot H_2O$, $KOH \cdot H_2O$ and $Sr(OH)_2 \cdot 8\ H_2O$ is evidently due to the diminishing O–O distances in these cases and the correspondingly large interactions between the hydroxyls and the water molecules contiguous to each other. The diminution of the frequency shifts of the water bands in $Sr(OH)_2 \cdot 8\ H_2O$ and $Ba(OH)_2 \cdot 8\ H_2O$ (from the normal value of 3655 cm.$^{-1}$ observed for water vapour) is also presumably due to analogous causes.

4. The Low-Frequency Region of the Spectrum

In the present section, we shall discuss the cases for which lattice frequency shifts are reported.

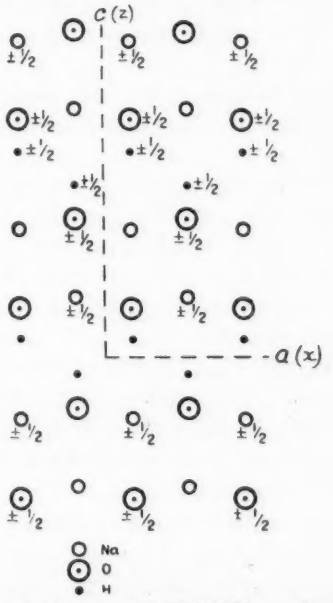
(i) *Lithium hydroxide monohydrate*.—The total number of vibrations to be expected in the Raman effect according to theory is 18. Amongst these are included the single symmetric internal vibration of the hydroxyls and three others due to the water present in the structure. Hence, fourteen vibrations should appear in the low-frequency region. However, it should be remarked that since $LiOH \cdot H_2O$ dehydrates easily to become LiOH when heated in an atmosphere of hydrogen below 140° C. (Partington, 1958),[18] the binding of the water molecules in the lattice is weak and the translational and rotational frequencies due to them will be rather low. It had not been possible to observe them. On the other hand, the binding between Li and OH should be quite strong as is evidenced by the high melting point of LiOH (450° C.). If we ignore the water molecules, there should appear in the Raman effect eight lattice frequency shifts, of which only five could be observed.

(ii) *Sodium hydroxide*.—The group characters and selection rules of the various irreducible representations of the group D_{2h}, to which NaOH belongs, are reproduced in Table II following. Figure 1 in the text illustrates the structure of NaOH.

TABLE II

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	Activity
A_g ..	1	1	1	1	1	1	1	1	R.E. only
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	R.E. only
B_{2g} ..	1	−1	1	−1	1	−1	1	−1	R.E. only
B_{3g} ..	1	−1	−1	1	1	−1	−1	1	R.E. only
A_u ..	1	1	1	1	−1	−1	−1	−1	Inactive in both
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	I.R. only
B_{2u} ..	1	−1	1	−1	−1	1	−1	1	I.R. only
B_{3u} ..	1	−1	−1	1	−1	1	1	−1	I.R. only
U_R ..	6	6	0	0	0	0	6	6	

U_R = number of atoms invariant under the group operation.
x, y, z correspond to the crystallographic axes a, b and c respectively.



TEXT-FIG. 1. Projection of the structure of NaOH in a plane normal to the b-axis. $\pm\frac{1}{2}$ indicate that the atoms are at the levels $\pm\frac{1}{2}b$. The remaining atoms are in the plane passing through the origin.

TABLE III

Class	n_i	T	T′	R	n_i'	Activity
A_g ..	3	0	2	0	1	R.E.
B_{1g} ..	0	0	0	0	0	R.E.
B_{2g} ..	3	0	2	1	0	R.E.
B_{3g} ..	3	0	2	1	0	R.E.
A_u ..	0	0	0	0	0	Inactive
B_{1u} ..	3	1	1	0	1	I.R.
B_{2u} ..	3	1	1	1	0	I.R.
B_{3u} ..	3	1	1	1	0	I.R.

n_i = Total number of vibrations; T = pure translations; T′ = Translational oscillations; R = rotational oscillations; n_i' = number of hydroxyl vibrations.

Table III shows the distribution of the several frequencies under the various classes. Group theoretical analysis shows that there should appear in the Raman effect 9 vibrations, *i.e.*, three each under the classes A_g, B_{2g}, and B_{3g}. We have already seen that the symmetric internal vibration of the hydroxyls belongs to class A_g. Since the three pure translations of the unit cell belong to the classes B_{1u}, B_{2u} and B_{2u} and since no rotational oscillations can occur about the two-fold axis $C_2(z)$ owing to the hydroxyl groups lying parallel to it, the remaining two vibrations under A_g should be of the translatory type. These can be described as arising from the translatory movements of the sodiums and hydroxyls along the z-axis and symmetrically with respect to the centre of inversion. Considerations analogous to the above show that there should be one rotational oscillation under each one of the classes B_{2g} and B_{3g}, the rotations of the hydroxyl groups being respectively about the y and x-axes. Also, there occur two oscillations under each one of the classes B_{2g} and B_{3g} due to the translatory movements (symmetrically with respect to the centre of inversion) of the Na's and OH's along the x and y-axes respectively.

Contrary to the theoretically expected number of eight, only five frequency shifts have been observed. However, a tentative explanation for the smaller number of observed shifts can be offered. The unit cell parameters determined by Ernst for NaOH show that for this orthorhombic

structure the lattice constants a and b are equal to each other within the limits of experimental error. Hence, each of the double layers possesses tetragonal symmetry, the four-fold axis (*i.e.*, c-axis) being shifted by $a/2$ as we pass from one double layer to another. If we neglect the weak coupling between the double layers which are far apart, it may easily be seen that the translatory movements along x and y axes (and also the rotational oscillations about the x and y-axes) would be of nearly the same frequency. In other words, the corresponding frequencies coming under the classes B_{2g} and B_{3g} would fall too close to each other to be resolved and only five frequencies would be observed.

The assignments of the individual frequency shifts to specific symmetry modes are arrived at from the following considerations. Even though each Na is surrounded by five hydroxyls, it is the hydroxyl nearest to it (along the z-axis) which can be identified as forming the NaOH group, the other group in the unit cell being related to it by the centre of inversion. (For the sake of convenience we shall describe here only the movements of the atoms in one group, the movements in the other being such that the vibration is symmetric with respect to the centre of inversion.) The translatory oscillations of Na and OH ions can actually be divided into (i) the movements of the Na and the hydroxyl against each other and (ii) the movement of the NaOH group as a whole. The former would be of high frequencies and amongst them the movement of the Na against the OH along the z-axis would be of highest frequency and hence the shift at 380 cm.$^{-1}$ is identified with this mode (A_g). Similar translatory oscillations of the Na's and OH's of the unit cell with their displacements parallel to the x and y axes would be of lower frequency and the frequency shift at 291 cm.$^{-1}$ therefore represents these modes (B_{2g} and B_{3g}). The translatory movements of the NaOH group as a whole parallel to the x, y and z axes would be of low frequencies and are to be identified with the shifts 98 and 114 cm.$^{-1}$ Amongst these, the more intense line at 98 cm.$^{-1}$ conceivably arises due to the overlap of the modes B_{2g} and B_{3g} involving movements parallel to x and y axes and the other shift at 114 cm.$^{-1}$ due to movements normal to the layer (A_g). The rather strong shift at 215 cm.$^{-1}$ is identified with the rotational oscillations about the y and x-axes (*i.e.*, classes B_{2g} and B_{3g}) since rotational oscillations of anisotropic groups usually give rise to strong Raman shifts. The appearance of the translatory oscillations with adequate intensity is due to the coupling generally present between translatory and rotatory symmetry modes.

Sodium hydroxide undergoes a structural transformation at about 300° C. The crystal structure of the high temperature form is not known. Whether the exceptionally large widths of the lines 215 cm.$^{-1}$ and 380 cm.$^{-1}$

are connected with this transformation (as in the case of the 206 cm.$^{-1}$ Raman line in α-quartz) is not quite clear.

(iii) *The monohydrates of sodium and potassium hydroxides.*—As a result of the numerous groups present in the unit cells of these two crystals, the number of lattice vibrations theoretically Raman active in the case of $NaOH.H_2O$ and $KOH.H_2O$ is quite large, being respectively 56 and 28. Nine lattice frequencies have been observed in $NaOH.H_2O$ and eight in $KOH.H_2O$. The following are plausible reasons for the small number of shifts observed. (i) Several of the allowed lines may be inherently weak. (ii) The large separation between the groups as in the case of the layered structure of $NaOH.H_2O$ indicates that the number of actual units that are responsible for the observed frequencies might be fewer than that rigorously considered. (iii) As is evident from the fact of the low transition points of the hydrates, the water molecules are feebly bound to the structure and their translatory and rotatory movements would be of very low frequencies and weak intensities. From a comparison of the spectrum of $NaOH.H_2O$ with that of NaOH it may be seen that there exists a correspondence between some of the frequencies. In particular, the intensities of the shifts 240 cm.$^{-1}$ in $NaOH.H_2O$ and 220, 232 cm.$^{-1}$ in $KOH.H_2O$ and their correspondence to the strong 215 cm.$^{-1}$ shift in NaOH indicate that they also arise most probably due to the rotational oscillations of the hydroxyls. The shifts at 213 and 243 cm.$^{-1}$ observed in $LiOH.H_2O$ may also be due to the rotational oscillations of the hydroxyls.

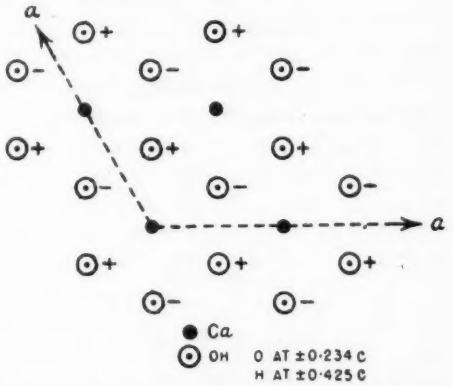
(iv) *Calcium hydroxide.*—In view of the fact that $Ca(OH)_2$ figures in our discussions in Part III also, the group characters and selection rules of the irreducible representations of the group D_{3d} to which it belongs are reproduced in Table IV. In it are also shown the number of vibrations under the different classes and their resolution into the translatory, rotatory and internal oscillations. Figure 2 in the text illustrates the structure of $Ca(OH)_2$.

Group theoretical analysis shows that the Raman spectrum should exhibit four frequency shifts, two each under the classes A_{1g} and E_g. We have already identified the internal vibrations of the hydroxyls symmetrically with respect to the centre of inversion as belonging to A_{1g}. The remaining frequency under A_{1g} represents the translatory movements, along the *c*-axis, of the hydroxyls symmetrically with respect to the centre of inversion. Similar symmetric translational oscillations of the hydroxyls in the plane perpendicular to the *c*-axis fall under the doubly degenerate class E_g. The rotational oscillations of the hydroxyls about any axis lying in the plane

TABLE IV

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	n_i	T	T′	R	n_i'	Activity
A_{1g} ..	1	1	1	1	1	1	2	0	1	0	1	R.E. only
A_{2g} ..	1	1	−1	1	1	−1	0	0	0	0	0	Inactive in both
E_g ..	2	−1	0	2	−1	0	2	0	1	1	0	R.E. only
A_{1u} ..	1	1	1	−1	−1	−1	0	0	0	0	0	i.a. both
A_{2u} ..	1	1	−1	−1	−1	1	3	1	1	0	1	I.R. only
E_u ..	2	−1	0	−2	1	0	3	1	1	1	0	I.R only
U_R ..	5	5	1	1	1	5						

R.E. = Raman effect; I.R. = infra-red; i.a. = inactive.



TEXT-FIG. 2. Projection of the structure of $Ca(OH)_2$ in a plane normal to the *c*-axis. + and − indicate the levels of the atoms. The hydroxyl groups are parallel to *c*. The Ca atoms are in the plane passing through the origin.

perpendicular to the *c*-axis belong to the class E_g. The calciums do not take part in any of the Raman active vibrations owing to their being located at the centres of inversion.

As indicated by theory, in the case of $Ca(OH)_2$ three lattice frequency shifts are observed at 247, 282 and 359 $cm.^{-1}$ The observed shifts, however, fall within too limited a range of frequencies to permit their identification with specific symmetry modes.

(v) *Octahydrated hydroxides of strontium and barium.*—Since the lattice spectra of $Sr(OH)_2 \cdot 8\,H_2O$ and $Ba(OH)_2 \cdot 8\,H_2O$ exhibit respectively only eight and nine frequency shifts (which are far fewer than would be indicated by the presence of the large number of groups in the unit cell) and also since the positions of the hydrogen atoms have not been determined, no attempt is made here to enumerate the frequencies theoretically. The reasons advanced in the cases of $NaOH \cdot H_2O$ and $KOH \cdot H_2O$ for the meagreness of the results observed in this region of the spectrum apply equally well to these cases also.

The unit cell parameters of $Ba(OH)_2 \cdot 8\,H_2O$ are given by $a = 9{\cdot}35$; $b = 9{\cdot}28$; $c = 11{\cdot}87$ A.U., and $\beta = 99°$. The substance exhibits a small optic axial angle of 8° 33′. The unit cell dimensions of $Sr(OH)_2 \cdot 8\,H_2O$ are $a = 9{\cdot}00$; $c = 11{\cdot}58$ A.U. and are comparable to that of $Ba(OH)_2 \cdot 8\,H_2O$. It appears highly likely that the structure of $Ba(OH)_2 \cdot 8H_2O$ is only a slightly distorted version of $Sr(OH)_2 \cdot 8\,H_2O$ and hence a comparison of their spectra is of interest.

In the lattice frequency region and in the high frequency region as well, a fair agreement between the frequency shifts of $Ba(OH)_2 \cdot 8\,H_2O$ and $Sr(OH)_2 \cdot 8\,H_2O$ may be noticed to exist. An explanation for the correspondence between the two spectra is possible since the unit cell parameters in the two cases are comparable and also since the monoclinic group C_{2h} to which $Ba(OH)_2 \cdot 8\,H_2O$ belongs is a subgroup of the tetragonal group D_{4h} of $Sr(OH)_2 \cdot 8\,H_2O$. From the point of view of Raman effect studies, only the following correlations existing between the five symmetric representations of D_{4h} and the two symmetric representations of C_{2h} are of interest. They are: (1) $A_{1g} \rightarrow A_g$; (2) $A_{2g} \rightarrow B_g$; (3) $B_{1g} \rightarrow A_g$; (4) $B_{2g} \rightarrow B_g$; (5) $E_g \rightarrow A_g + B_g$. In the group D_{4h} only the four symmetric classes A_{1g}, B_{1g}, B_{2g} and E_g are Raman active, A_{2g} being inactive. In C_{2h} both A_g and B_g are Raman active. Hence, as a result of the lowering of the symmetry from D_{4h} to C_{2h} the inactive vibrations corresponding to A_{2g} of D_{4h} become active and the doubly degenerate vibrations (E_g) split into two. The lines under the totally symmetric class are often observed to be of considerable intensity. The transformation of B_{1g} of D_{4h} into A_g of C_{2h} might hence mean that the corresponding line observed with the substance of lower symmetry would appear with enhanced intensity. The appearance of the hydroxyl frequency at 3529 $cm.^{-1}$ rather strongly in $Ba(OH)_2 \cdot 8\,H_2O$ in contrast to its weak counterpart at 3536 $cm.^{-1}$ in $Sr(OH)_2 \cdot 8\,H_2O$ is therefore intelligible. The appearance of doublets in the lattice spectrum of $Ba(OH)_2 \cdot 8\,H_2O$ corresponding to single frequencies observed in $Sr(OH)_2 \cdot 8\,H_2O$ (*e.g.*, 230 → 205–220; 297 → 276 to 287) is obviously due to the splitting arising from the

removal of degeneracy. Here again, the two frequencies 205 and 220 cm.$^{-1}$ (corresponding to the line 215 cm.$^{-1}$ due to rotational oscillations of the hydroxyls in NaOH) represent the rotational oscillations of the hydroxyls, the former which is more intense belonging to the class A_g and the latter to B_g. The frequency shifts 230 and 297 cm.$^{-1}$ belong to the doubly degenerate class E_g of D_{4h}. It is evident that these corresponding frequencies represent predominantly the translatory and rotatory oscillations of the hydroxyls since the vibrations in which the bariums and strontiums participate would be of different frequencies owing to the large difference in their atomic masses.

The author's grateful thanks are due to Professor Sir C. V. Raman, F.R.S., N.L., for the valuable discussions he had with him.

5. Summary

The paper discusses the results reported in Part I in relation to the crystal structures of the substances. From a comparison of the facts with the theoretically expected picture of the spectrum, the salient features exhibited by the spectra have been explained, in addition to identification and assignment of the frequencies wherever feasible. The progressive variations in the hydroxyl shifts exhibited by the different hydroxides and their hydrates are explicable as due to the interactions of the hydroxyls with each other and also with their neighbouring water molecules in the case of the hydrates.

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THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

Part III. Discussion of the Infra-red Data

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1. Introduction

Comparatively few investigations on the infra-red spectra of the hydroxides appear to have been made and even these mainly concern themselves with the 3 μ region. In the present part we shall discuss the data available for LiOH, $LiOH.H_2O$, NaOH, $Ca(OH)_2$ and $Mg(OH)_2$. Duval and Lecomte (1941) had reported the infra-red spectra of LiOH, $Ca(OH)_2$, $Mg(OH)_2$ and $Al(OH)_3$ for the region 600–1600 cm.$^{-1}$ which falls outside the range of even the first order combinations of most of the lattice frequencies of these substances. In many of the cases studied by them there appear strong maxima in the region of 880 cm.$^{-1}$ and 1440 cm.$^{-1}$ corresponding to the strong absorption maxima usually observed with the carbonates. In view of the meagreness of the data for the lattice frequencies active in the infra-red and also since it appears to us that the substances used by Duval and Lecomte in their study have been contaminated by the atmospheric carbon dioxide to form the carbonates, we do not propose to discuss their data.

2. The Infra-red Spectra of LiOH, $LiOH.H_2O$ and NaOH

(i) *$LiOH$ and $LiOH.H_2O$.*—The infra-red absorption spectra of LiOH and $LiOH.H_2O$ have been recorded by Jones (1954) in the 3 μ region using thin films of the substances, the frequencies of the absorption maxima of the OH vibrations being respectively 3678 and 3574 cm.$^{-1}$ The internal vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion in these two cases belong respectively to the classes A_{2u} of D_{4h} and B_u of C_{2h} and are in each case the only infra-red active internal mode theoretically possible and hence the respective maxima at 3678 and 3574 cm.$^{-1}$ are to be identified with them. That the infra-red frequencies in these cases are only slightly different from the Raman active frequencies is indicative of weak coupling between the hydroxyls. The diminution of the hydroxyl frequency in $LiOH.H_2O$ by about 100 cm.$^{-1}$ is hence largely to be attributed

to the proximity of the water molecules to the hydroxyls. Two other maxima at 3000 cm.$^{-1}$ and 1586 cm.$^{-1}$ respectively due to the stretching and bending vibrations of the water molecules in $LiOH \cdot H_2O$ have also been reported by him, the diminution in their frequencies being due to causes already discussed.

An absorption maximum at 7195 cm.$^{-1}$ has also been observed by Jones in LiOH and identified as the overtone of 3678 cm.$^{-1}$ According to theory this overtone is forbidden in the infra-red and only the combination between the Raman active (3664 cm.$^{-1}$) and the infra-red active (3678 cm.$^{-1}$) vibrations is allowed in the infra-red. Anharmonicity can be expected to be the cause of the violation of the selection rules. The large difference (161 cm.$^{-1}$) between the anticipated value for the overtone and the observed value indicates the presence of considerable mechanical anharmonicity. However, further studies are required to elucidate this feature more fully.

(ii) *Sodium hydroxide*.—The infra-red absorption spectrum of NaOH in the form of thin films has been studied by Busing (1955) and a sharp maximum at 3637 cm.$^{-1}$ is reported by him. This is to be identified with the theoretically expected infra-red active internal vibration of the hydroxyls antisymmetrically with respect to the centre of inversion and belonging to the class B_{1u} of D_{2h}. The small difference of 5 cm.$^{-1}$ between the Raman active and infra-red active hydroxyl frequencies indicates that the coupling between the hydroxyls is very weak.

3. THE INFRA-RED SPECTRA OF $Ca(OH)_2$ AND $Mg(OH)_2$

Unlike the above cases, the infra-red spectra of $Ca(OH)_2$ and $Mg(OH)_2$ exhibit complex structures in the 3 μ region and it was therefore suspected that the actual unit cell of the structure should be larger than that derived from X-ray studies (Mara and Sutherland, 1953). However, reinvestigations of the structures by both X-ray and neutron diffraction methods have only revealed the correctness of the structure proposed earlier. So far, only tentative explanations have been offered for the complex features of the spectra.

It has already been shown in Table IV of Part II that in the cases of $Ca(OH)_2$ and $Mg(OH)_2$, there are possible four infra-red active fundamentals of which one is due to the internal vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion and three others are due to translatory and rotatory oscillations. Besides these, the selection rules for combinations and overtones indicate that the combinations between the Raman active fundamentals and the infra-red active fundamentals (*viz.*, $A_{1g} \times A_{2u}$;

$A_{1g} \times E_u$; $E_g \times A_{2u}$; $E_g \times E_u$) are allowed in the infra-red. The first overtones and first order combinations of the infra-red active frequencies between themselves and similarly the combinations and overtones of the Raman active frequencies are forbidden in infra-red absorption. An absorption maximum can be identified as a combination of the differential type only if the corresponding summational is also observed. The complex features exhibited by the spectra of $Ca(OH)_2$ and $Mg(OH)_2$ are explicable on the basis of these criteria.

(i) *Calcium hydroxide.*—The infra-red absorption spectrum of $Ca(OH)_2$ has been reported by Busing and Morgan (1957). Table I shows the frequencies of the absorption maxima and the nature of their origin. The

TABLE I

Absorption maxima in $Ca(OH)_2$ and their interpretation

Absorption maximum in cm.$^{-1}$	Their suggested origin	Calculated value in cm.$^{-1}$
4164	3616+282+263	4161
3932	3644+282; 3616+322	3926; 3938
3899	3644+247	3891
3877	3616+263	3879
3720	3616+98	3714
3644	A_{2u}	..
3629*	?	..
3523	3616−98	3518
3364	3644−282	3362
3333†	3616−263	3353
3294	3616−322	3294
3073	3616−282−263	3071

* Very weak; † See text for alternative explanation.

prominent maximum at 3644 cm.$^{-1}$ observed by them, when the crystal is orientated such that the incident beam is inclined to the *c*-axis, represents the hydroxyl stretching vibrations (antisymmetrically with respect to the centre of inversion) under the class A_{2u}. The numerous other maxima are explicable as arising due to (i) the combinations of the frequency 3644 cm.$^{-1}$ with the Raman active lattice frequencies, and (ii) combinations of the Raman active frequency 3616 cm.$^{-1}$ with the infra-red active lattice frequencies. The actual interpretation of the facts was arrived at by considering the combinations of the former type first and then by choosing from amongst the remaining maxima those pairs of frequencies whose mean value was near 3616 cm.$^{-1}$ By this process it was possible to discover also the three lattice frequencies (98, 263 and 322 cm.$^{-1}$) active in the infra-red. The calculated and observed values shown in Table I are in fair agreement except for the frequency at 3333 cm.$^{-1}$ The only other explanation that could be given for this maximum, without disturbing the consistent scheme of assignments arrived at for the other frequencies, is that it is a combination, forbidden by selection rules, *viz.*, 3616−282; the corresponding summational (3616 + 282) is also observed at 3899 cm.$^{-1}$ The infra-red activities of these are presumably to be attributed to their contiguity to strongly active infra-red frequencies. The appearance of the Raman frequency 282 cm.$^{-1}$ in combinations (differential and summational) with the infra-red active frequency of 3644 cm.$^{-1}$ vindicates our earlier identification of it as a genuine Raman shift of $Ca(OH)_2$.

(ii) *Magnesium hydroxide.*—The infra-red absorption spectrum of $Mg(OH)_2$ has been investigated in detail recently by Mara and Sutherland (1953) and also by Benesi (1959). Using fine powders Benesi has observed a single sharp intense absorption maximum at 3698 ± 2 cm.$^{-1}$ corresponding to the internal vibrations of the hydroxyls (antisymmetrically with respect to the centre of inversion) belonging to the class A_{2u}. Mara and Sutherland who used single crystals of $Mg(OH)_2$ report numerous maxima in addition to a maximum at 2·71 μ (corresponding to 3698 cm.$^{-1}$) which appears when the *c*-axis of the crystal is inclined to the incident beam. The explanation of the several maxima shown in Table II is rather indirect since neither the Raman active nor the infra-red active lattice frequencies have so far been observed. The numerous maxima arise evidently due to combinations, (i) between the Raman active frequency 3651 and three infra-red active lattice frequencies and (ii) between the infra-red active frequency 3698 cm.$^{-1}$ and the three Raman active lattice frequencies. These combinations should appear on either side of the frequency region 3651–3698, the mean value of the corresponding summational and differential frequencies being centred

TABLE II

Absorption maxima in $Mg(OH)_2$ and their interpretation

Observed maxima		Their suggested origin	Calculated values	
in μ	in cm.$^{-1}$		in cm.$^{-1}$	in μ
2·06	4854	Combinations of higher order	..	..
2·19	4566	do.	..	..
2·24	4464	3698+2×380	4458	2·243
2·32	4310	3651+380+293	4324	2·313
2·45	4082	3698+380	4078	2·452
2·47	4049	3651+390	4041	2·474
2·49	4016	3698+324	4022	2·486
2·53	3953	3651+293	3944	2·535
2·64	3788	3651+127	3778	2·647
2·71	3690	A_{2u}	..	..
2·74	3650	A_{1g} ?	..	..
2·83	3534	3651−127	3524	2·838
2·97	3367	3651−293; 3698−324	3358; 3374	2·978; 2·964
3·01	3322	3698−380	3318	3·014
3·06	3268	3651−390	3261	3·066
3·08	3247*	..	..	..

* See text for explanation.

about either 3651 or 3698 cm.$^{-1}$ The identification of the corresponding summational and differential frequencies is facilitated by the similarity of their behaviour in the spectra obtained for two different orientations of the crystal. For example, the maxima at 2·45 μ and 3·01 μ are observed only when the incident beam is perpendicular to the *c*-axis and not when it is parallel to the *c*-axis.

The wavelengths of the absorption maxima are given by Mara and Sutherland to only two places of decimals and it can be seen that the frequency 3690 observed by them differs (by 8 $cm.^{-1}$) from the more accurate measurement of Benesi. In view of this possibility of errors of the order of 10 $cm.^{-1}$ in the observed values, the agreement between the calculated and observed values of Table II should be considered quite satisfactory. The analysis of data reveals that there should be observed in the case of $Mg(OH)_2$ the following lattice frequencies: (*a*) 324 and 380 $cm.^{-1}$ in the Raman effect; (*b*) 127, 293 and 390 $cm.^{-1}$ in the infra-red absorption. The value of the third Raman active lattice frequency might probably be 451 $cm.^{-1}$ as shall be seen below. It is possible to explain the maximum observed at 3247 $cm.^{-1}$ as a differential, *i.e.*, 3698—451, the frequency 451 $cm.^{-1}$ being assumed to be of the Raman active type. In that case, the corresponding summational also should be observed at 4149 $cm.^{-1}$, *i.e.*, at 2·41 μ. But, such a maximum has not been observed, probably because of its falling close to the strong absorption at 2·45 μ and being obscured by it. However, the above is only a tentative explanation. It is rather surprising that there should be observed at 3650 $cm.^{-1}$ in the infra-red, a frequency closely agreeing with the Raman active frequency, in violation of the rule of mutual exclusion.

The crystal structure of $Mg(OH)_2$ is a more closely packed one than that of $Ca(OH)_2$ as is evident from a comparison of their lattice constants, which are given by:

(i) $Mg(OH)_2$: $a = 3{\cdot}12$; $c = 4{\cdot}73$ A.U.

(ii) $Ca(OH)_2$: $a = 3{\cdot}59$; $c = 4{\cdot}91$ A.U.

Consequently, the interionic forces in $Mg(OH)_2$ would be stronger than in $Ca(OH)_2$ and the fact that the lattice frequencies of $Mg(OH)_2$ are higher than those of $Ca(OH)_2$ is therefore not surprising. The lower atomic mass of Mg would also be responsible for higher frequencies, in the case of modes involving movements of the magnesiums.

It is interesting to note that in all the cases discussed herein, the infra-red active hydroxyl frequencies are always higher than the Raman active hydroxyl frequencies. In the latter case, the dipole moments produced at the two hydroxyls related by the centre of inversion are opposite to each other resulting in their cancellation and hence the vibration is infra-red inactive. On the other hand, in the case of the infra-red active vibrations, the dipole moments produced at the two hydroxyls are additive. Because of the fact that there is a displacement of charge, or in other words, a polarization of the medium taking place in the case of the infra-red active vibration, the potential energy and hence the restoring force for this mode is

greater than in the case of the Raman active mode. The higher value of the infra-red active hydroxyl frequency is hence intelligible.

In conclusion, the author wishes to express his deep sense of indebtedness to Professor Sir C. V. Raman, F.R.S., N.L., for the encouragement and valuable suggestions that he gave during the course of this investigation.

4. Summary

In each of the cases of LiOH, $LiOH \cdot H_2O$, NaOH, $Ca(OH)_2$ and $Mg(OH)_2$ the stretching vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion give rise in infra-red absorption to a single sharp intense maximum at about 3650 $cm.^{-1}$ as is to be theoretically expected. In all cases, the infra-red active hydroxyl frequency is found to be higher than the corresponding Raman active mode and the origin of this feature is explained.

The spectrum of $Ca(OH)_2$ recorded with single crystals exhibits on either side of the principal maximum due to the hydroxyl vibration, numerous other maxima which have hitherto remained unexplained. Some of them arise due to combinations between the observed Raman active lattice frequencies and the infra-red active hydroxyl frequency. The rest are explicable as combinations between the Raman active hydroxyl frequency and infra-red active lattice frequencies. Features similar to those observed in the spectrum of $Ca(OH)_2$ are exhibited by $Mg(OH)_2$ also, and have been explained in an analogous fashion. No experimental data regarding the infra-red active lattice frequencies of $Ca(OH)_2$ and the Raman active and infra-red active lattice frequencies of $Mg(OH)_2$ are available. The values of these are also revealed by the above analysis.

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HALOGEN NUCLEAR MAGNETIC RESONANCE SHIFTS

Part I. Cl^{35} Resonance in Alkali Chlorides

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Abstract

The nuclear magnetic resonance shifts (chemical shifts) of Cl^{35} in aqueous solutions of alkali chlorides were determined using a High Resolution NMR Spectrometer. These small shifts probably represent the effect of the neighbouring atom even in the highly ionic state. A similarity of these results to the quadrupole coupling constants of the halogen atom in these molecules is pointed out.

Introduction

Determinations of nuclear magnetic resonance shifts (chemical shifts) are of great help in elucidating some of the interesting properties of the electronic distribution in molecules.[1–5] In the present experiments chemical shifts Cl^{35} resonance were determined in some compounds, of which the results of alkali chlorides will be presented in this paper. The NMR signals of Cl^{35} would, in general, be broad,[6] due to quadrupole interactions. Masuda[7] has determined the chemical shifts in four liquid chlorine compounds $TiCl_4$, $VOCl_3$, CrO_2Cl_2 and $SiCl_4$, and found the line widths to be proportional to the square of the quadrupole coupling constants, showing that the quadrupole interactions form the dominant relaxation mechanism. But the line widths are less in the case of aqueous solutions of alkali chlorides where these interactions are minimum.

The experimental details and the results obtained are presented in the next two sections. In the last section the results are discussed in comparison with the quadrupole coupling constants of these molecules in gaseous phase.

Experimental Arrangement

The chemical shifts were measured on a Varian V-4300 B High Resolution NMR Spectrometer, using a 12″ electromagnet. The power supply

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for the magnet has voltage and current regulation, and the drifts in the field, occurring due to temperature variations, etc., are compensated by a " Superstabilizer ". The overall stability and homogeneity of the static magnetic field is roughly 1 part in 10^7 or better. The spectrometer essentially consists of 3·6 Mc. fixed frequency transmitter and receiver units with the associated probe, and a sweep unit providing for variable sweep field of adjustable frequency. The corresponding value of the static magnetic field for Cl^{35} magnetic resonance is about 8,627 gauss. The frequency stability of the R.F. unit is about 1 part in a million per hour. A Dumont Model 304-AR Oscilloscope is used for visual observation of the resonances, and a Sanborn Model 151-100 A Recorder is employed for recording them. For recording, a " Slow-Sweep Unit " is provided along with the Superstabilizer with which the magnetic field can be varied either way, linearly, at a slow and variable rate. The sample, in liquid form, is contained in a pyrex glass tube of about 13 mm. o.d., with a reference sample in another glass tube of about 7 mm. o.d., placed inside. Thus the signals from the sample and reference are simultaneously observed. The measurement was carried out by the side-band technique,[8] using Hewlett-Packard Model 200 B Audio Oscillator to modulate the sweep voltage. The frequency of the Audio Oscillator is accurately determined by calibrating with the proton resonance spectrum of ethanol at 40 Mc. The error involved in this determination is about $\pm$ 2 cps.

The signals obtained for RbCl with NaCl as the reference, along with the side-bands separated by 184 cps., on either side, from the main signals, are shown in Fig. 1. Figure 2 shows the signals for LiCl and CsCl.

The chemical shift is usually expressed as

$$\delta = \frac{H_c - H_r}{H_r} \times 10^5,$$

where δ is the chemical shift, H_c and H_r are the values of the magnetic field at which the resonance occurs in the compound of interest, and the reference compound respectively.

Results

The chemical shifts for Cl^{35} magnetic resonance in alkali chlorides are shown in Table I.

Measurements were made on the aqueous solutions of these compounds. The values are given with respect to sodium chloride as the reference. The shifts in the case of LiCl and KCl were not measured with NaCl as the reference, but they were measured with respect to CsCl and the values were finally

TABLE I

Compound	Chemical shift δ	Observed $eQq_{molecule}$[17] in Mc.	$(D-i)\beta$ eQq_{atom}[17] in Mc.
LiCl ..	$-0\cdot31\pm0\cdot1$	..	..
NaCl ..	0	<1	..
KCl ..	$-0\cdot18\pm0\cdot1$	0·04	0·51
RbCl ..	$-1\cdot05\pm0\cdot1$	0·774	1·24
CsCl ..	$-2\cdot32\pm0\cdot1$	3·00	3·00

reduced to NaCl as the reference. The bulk diamagnetic susceptibility correction was not applied.* All the measurements were carried out at room temperature. Measurements were done with different concentrations of the solutions, but the shifts were found to be independent of the concentration, within the experimental accuracy of about $\pm 0\cdot1$ in the chemical shift.

DISCUSSION

Ramsey[9] has shown that the chemical shift arises due to interaction between the molecular electrons and the external magnetic field. The interaction would, in turn, produce a small magnetic field at the site of the nucleus in opposition to the external field. The magnitude of this shielding field is different in different molecules due to variations in electronic structure.

If the alkali halides are 100% ionic, the shielding field for the halogen nucleus or the alkali nucleus, according to Ramsey's theory, would not vary from molecule to molecule, and hence no chemical shift would be observed between these molecules. However, Gutowsky and MacGarvey[10] have observed chemical shifts between the solid Rubidium and Cesium halides for Rb^{87} and Cs^{133} resonances. Recently, Bloembergen and Sorokin[11] have observed the shifts for both halogen and alkali nuclei in the case of solid Cesium halides. Kanda[12] has also observed halogen resonance shifts in certain solid metal halides. In all these cases, the observed shifts were explained by attributing a certain amount of covalent character to the crystalline bonds in these halides.[10–13] The present work shows the occurrence of the shifts in Cl^{35} resonance in aqueous solutions of alkali chlorides

* The correction will not bring any significant difference in the results, as it would be within the experimental error involved in the measurements.

where crystalline fields are not expected. The shifts observed here are much smaller in magnitude than those in solid samples mentioned above.

Shoolery and Alder[18] observed the proton magnetic resonance shifts in various aqueous electrolytes, and the fluorine magnetic resonance in aqueous potassium fluoride solutions at several concentrations. They found concentration dependence of these shifts and explained on the basis of solvention interactions. The overall effect of these interactions, if any, are probably negligible in the alkali chloride solutions worked out in the present experiments, as the shifts are found, within experimental errors, to be independent of concentration.

It is interesting to note the similarity of the nuclear magnetic resonance shifts in the present experiment to the known quadrupole coupling constants of these molecules in gaseous phase. The similarity can be expected[7, 14] as both these depend upon the fraction of unbalanced *p*-character about the atom in question. The quadrupole coupling constant for a halogen atom forming a hybrid bond, with a negative ionic character of amount β is given by[15]

$$eQq_{\text{molecule}} = (-1 + \alpha - S^2)(1 - \beta)\, eQq_{\text{atom}}$$

where α is the hybridization, S is the overlap factor and eQq_{atom} is known from atomic data.[16] It can be seen from this expression that eQq_{molecule} would be zero if the ionic character is 100%. The observed values of the quadrupole coupling constants, in the gaseous phase, of KCl, RbCl, and CsCl, were explained by Vankateswarlu and Jaseja[17] by modifying the above expression as

$$eQq_{\text{molecule}} = [(-1 + \alpha - S^2)(1 - \beta) + (D - i)]\, \beta\, eQq_{\text{atom}}$$

where D represents the effect on quadrupole coupling constant due to distortion of the closed shells of the halogen atom, and i represents the effect due to presence of adjacent ions or atoms in the molecule. The contribution of this term, $(D - i)\ \beta\, eQq_{\text{atom}}$, to the eQq_{molecule} as given by Venkateswarlu and Jaseja[17] is given in the fourth column of Table I.

It may be noted that the chemical shift for LiCl with reference to NaCl is towards the same direction as that for KCl, RbCl and CsCl. For comparison of this behaviour, the quadrupole coupling constant is not known for LiCl and it is not correctly found for NaCl. A similar behaviour can, however, be noted in the case of quadrupole coupling constants of bromine and iodine in the bromides and iodides of Lithium, Sodium and Potassium.[17]

The concentration independence of the observed nuclear magnetic resonance shifts, and the similarity of the trend of variation of these shifts to that of the corresponding nuclear quadrupole coupling constants, suggest the need of a quantitative explanation of these two effects on similar grounds in these molecules. However, more concrete conclusions would be attempted after the data on the other halides are collected.

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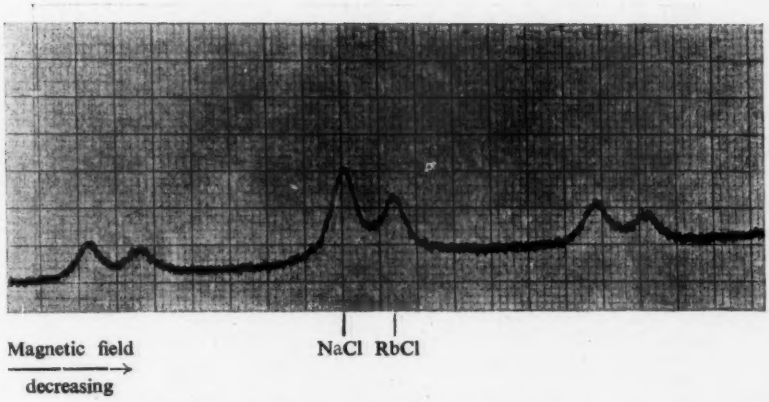

FIG. 1. Cl^{35} NMR signals from aqueous solutions of RbCl and NaCl (reference) with side bands separated by 184 cps. on either side of the main signals.

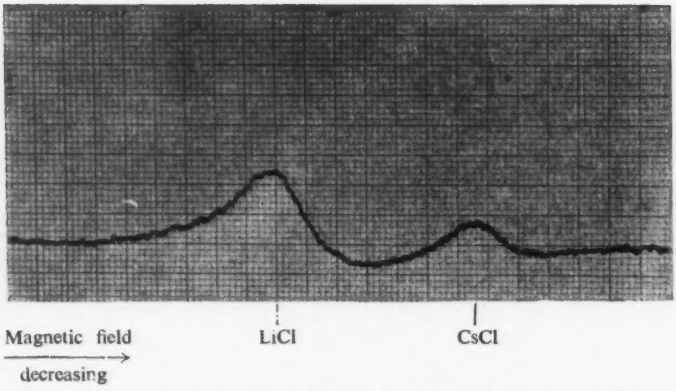

FIG. 2. Cl^{35} NMR signals from LiCl and CsCl (fast recording).

SPREAD-F IN THE IONOSPHERE OVER AHMEDABAD DURING THE YEARS 1954-57

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Abstract

From a study of spread-F or F-scatter at Ahmedabad during the four years 1954–57 of increasing sunspot activity, it was found that the time of its maximum occurrence receded from 03 hr. in low sunspot years to an hour or two before midnight in high sunspot years. This was particularly well seen in the winter and equinoctial months. Also, maximum spread-F activity which was found in summer in sunspot minimum years, occurred in equinoxes in maximum sunspot years. The frequency of occurrence of spread-F was found to be a maximum when hpF_2 was in the range 300–350 km. F-scatter and F_2-stratification were found to be anti-correlated both in their diurnal and seasonal variations. The general trend was towards decreased spread-F with increased sunspot activity.

It is concluded that (1) spread-F at Ahmedabad geomagnetic latitude ($\Phi = 13{\cdot}6°$ N) undergoes variations similar to those at equatorial stations, more so in high sunspot years, (2) the change-over from low-latitude type to middle-latitude type of variation of spread-F takes place at about geomagnetic latitude 22°, and (3) spread-F at Ahmedabad decreases with increase in magnetic activity, which is the reverse of that observed at high latitudes.

I. Introduction

Vertical radio pulses sent up into the ionosphere are sometimes reflected to earth not as sharp echoes, but return as a broad band of echoes consisting of a number of reflections of varying amplitudes. The broadness or the separation of such echoes depends on the structure of the irregularities and their distribution. Examples of ionograms depicting such echoes are given in *The Annals of the I.G.Y.*, Vol. III. They may take the following forms:—

(1) Forking of the cusp of the critical frequency,

(2) Slightly displaced parallel records with different critical frequencies,

(3) Diffuseness throughout the range of frequencies closely superposed on parallel records,

(4) Spreading confined to near the height of maximum electron density, and

(5) Completely diffused echoes with no sharp definition of the layer or cusp of critical frequency.

Eckersley (1940) and Dieminger (1951) have dealt with the possible mechanisms for spread-F. It is found from the Ahmedabad records that the major contribution to spread-F is due to irregularities in the F_2 layer and only a very small part is due to E_s. The phenomenon is mainly a night-time one. The present study deals with the diurnal and seasonal changes in the occurrence of spread-F at Ahmedabad (23° 02′ N, 72° 38′ E) in years of varying sunspot activity. Its relation to foF_2 and hpF_2 will also be discussed.

At latitudes higher than that of Ahmedabad, Reber (1954 *a*, *b*), Meek (1954) and Dagg (1957) have shown that there is a peak in the frequency of occurrence of F-scatter near 03 hr. in winter and that the number decreases with increase in sunspot number at middle latitudes but it increases at high latitudes, for example, at Winnipeg and Slough. At Brisbane, Singleton (1957) found that F-scatter had maximum occurrence in winter.

In equatorial latitudes, Osborne (1951) at Singapore found that scatter echoes begin to appear when the height of the F_2 layer decreases after passing a maximum value. The frequency of occurrence was found to be a maximum at about 20 hr. in the equinoctial months. At Ibadan, Wright and others (1956) reported the occurrence in the summer of low sunspot years of a peak around midnight. Wells (1954) at Huancayo found that F-scatter echoes were frequent between 20 and 04 hr. with a peak at about 03 hr. The occurrences were maximum in local summer, but in low sunspot years, there was a secondary maximum in winter. The general trend was a decrease in occurrence with increase in sunspot number. Bhargava (1958) reported that F-scatter variations at Kodaikanal in 1955–56 were similar to those at Singapore. Observations at Ahmedabad show that spread-F variations at this station are more like those at equatorial stations, particularly during high sunspot years. A summary of observations at various stations is given in Table I (*see* Appendix).

II. Monthly Frequencies of Occurrence of Spread-F at Ahmedabad in 1954 and 1956

The percentage of spread-F at a particular hour was calculated from the number of days when spread-F was observed and the total number of

days of usable records. Figures 1 and 2 give the total percentage of occurrence of all types of F-scatter echoes; the frequency of each type is not shown separately. They show the diurnal variation of F-scatter for each month of the low sunspot year 1954 and of the high sunspot year 1956 respectively. Since spread-F is rarely observed during daytime, only night hours are included. In these figures are also included the median values of foF_2 and hpF_2. In the year 1957 which had a still higher sunspot activity, the diurnal variation of spread-F was similar to that in 1956, but its frequency of occurrence had fallen down further.

1954

It can be seen from Fig. 1 that in all the months of the year 1954, the spread-F usually commenced at 20 hr. and ended at 06 hr. with a maximum at about 03 hr. The rate of fall in spread-F near sunrise was much sharper than the rate of increase after nightfall. Whatever was the degree of F-scatter during night hours, the *h'-f* trace became free from any spread-F after sunrise. An interesting point about spread-F is that corresponding to every fall in hpF_2, there is an increase of spread-F, particularly when the level is in the range 300–350 km. In 1954, spread-F was at a high level and hpF_2 was between 275 and 325 km., but in 1956 hpF_2 was between 325 and 375 km. The double peak of spread-F activity in winter months can be seen to be associated with two separate falls of hpF_2. The occurrence was most frequent in summer months, and it is seen that during these months hpF_2 remained in the 300–350 km. range for a longer time than in other months.

1956

If we examine Fig. 2 in which spread-F observations for the year 1956 are shown, it will be seen that some important changes took place after January 1956. The hour of peak of spread-F receded from 03 hr. to an hour or two before midnight, particularly in winter and equinoxes (*see* also Fig. 4) when the electron density (or foF_2) was still at a high value. The occurrence of a peak of spread F at pre-midnight hours in these months is associated with a fall in hpF_2 after 20 hr. and particularly when its value lay between 300 and 350 km. It may also be noted that maximum of hpF_2 which used to occur at midnight or an hour later in a year of low sunspots was found to take place at about 20 hr. in a high sunspot year, a fact which parallels changes in spread-F occurrence. The morning peak of spread-F vanished in the winter of 1956–57. There is no indication of any correlation between foF_2 and spread-F variations.

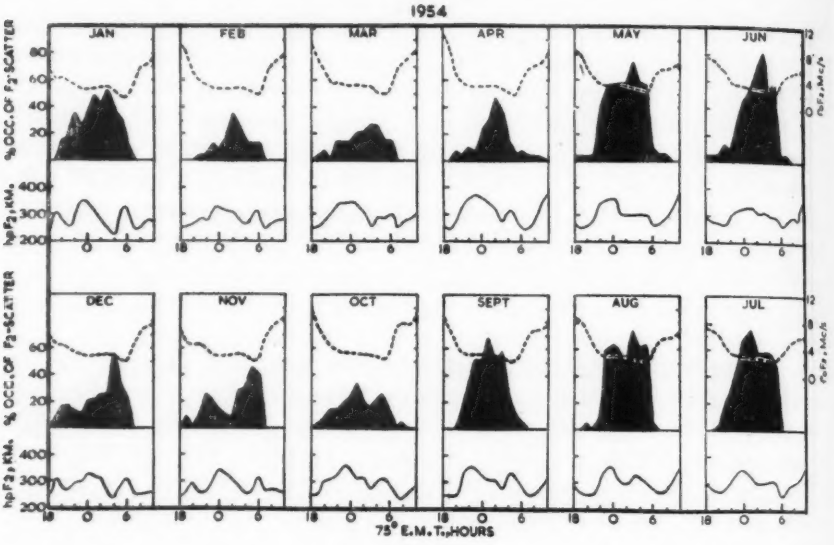

FIG. 1

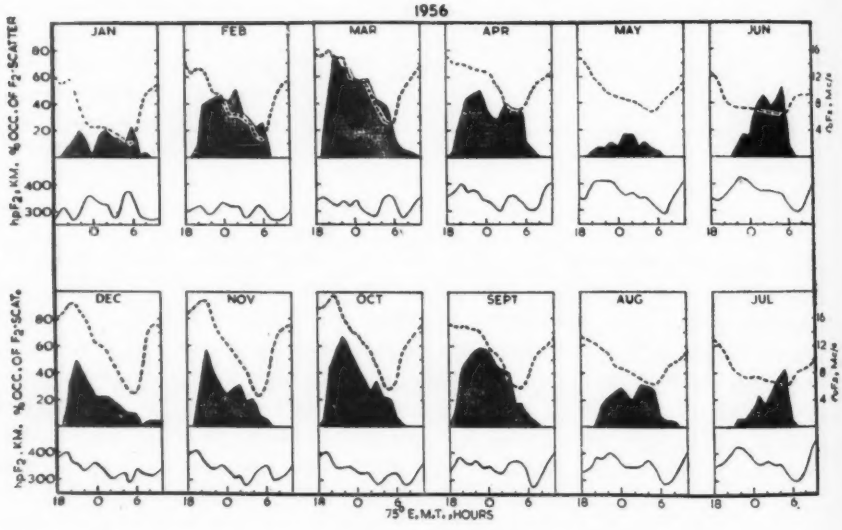

FIG. 2

FIGS. 1 and 2. Diurnal variation of occurrence of spread-F and median hourly values of foF_2 and hpF_2 at Ahmedabad in each month of (1) 1954, a sunspot minimum year and (2) 1956, a high sunspot year.

III. Progressive Changes of Spread-F from 1954 to 57

A picture summarising the variations of spread-F in different seasons through the half solar cycle 1954–57 is presented in Fig. 3 where each year is divided into three seasons (*viz.*, Winter: November, December, January and February; Equinox: March, April, September and October; Summer: May, June, July and August). In 1957, only November and December are included in the winter months, whereas in the other years, winter includes the first two months of the following year also. It is to be noted that marked changes in spread-F activity began in October 1955 when the sun-spot number began to increase rapidly.

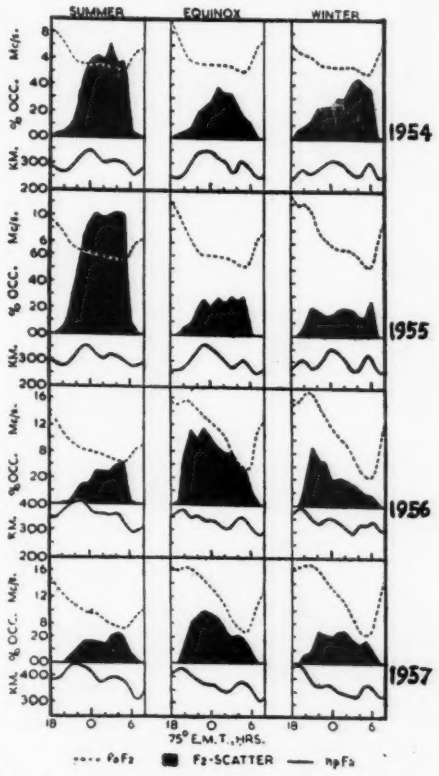

Fig. 3. Diurnal variation of spread-F at Ahmedabad in each season of the years 1954–57.

Winter.—On the whole, mean spread-F activity in winter did not change much from 1954 to 57. The only important change was that the time of

occurrence of the peak receded from post-midnight hour to pre-midnight hour.

Equinoxes.—In 1954–55, maximum spread-F was observed at about 03 hr. and in 1956–57 at about 21 hr. Spread-F was more frequent in the equinoctial months than in winter and summer in years of high sunspot activity.

Summer.—Great activity of spread-F was observed in the summer months of 1954–55, the maximum being in the summer of 1955. It was at a low level in the summer of 1956–57. The spread-F activity in summer of 1953 (not shown here) was even greater than in the summer of 1954. It appears that maximum F-scatter is observed in summer not quite at the sunspot minimum but on either side of the minimum of the sunspot cycle. At Huancayo also (Wells, 1954), the peak of spread-F occurred in the local summer of 1945–46 in the last sunspot cycle, that is after the year of minimum sunspot activity.

It is concluded that in high sunspot years, spread-F over Ahmedabad ($\Phi = 13{\cdot}6°$ N) has characteristics similar to those at other equatorial stations and differ from those at higher latitudes.

In Fig. 4 are shown the times of maximum of F-scatter in each month. The change of the hour of maximum from post-midnight in 1954–55 to pre-midnight and fluctuating hours in 1956–57 is clearly seen.

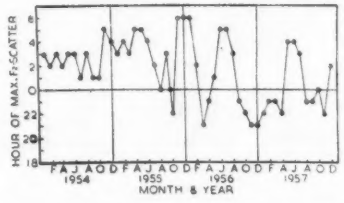

FIG. 4. Hours of maximum occurrence of spread-F over Ahmedabad in each month of the years 1954–57.

IV. SEASONAL, ANNUAL AND SUNSPOT CYCLE VARIATIONS OF SPREAD-F AT AHMEDABAD

Monthly mean values of spread-F frequencies between 20 and 06 hours, monthly mean magnetic character figures C_p and monthly median midnight values of hpF_2 and foF_2 are given in Fig. 5.

The seasonal variation of spread-F runs almost in opposite direction to that of C_p. The relationship is very clear in 1954 and 1955. In 1956 and 1957, the disturbances in C_p were so great that clear correlations cannot be

seen from the mean values. However, a detailed study of individual days has shown that an anti-correlation exists between spread-F and magnetic activity (Kotadia and Ramanathan, 1959). The results of this study will be published elsewhere. From the records of midnight hpF_2 and foF_2, it is not clear that there is any definite relation between these quantities and the variations of spread-F.

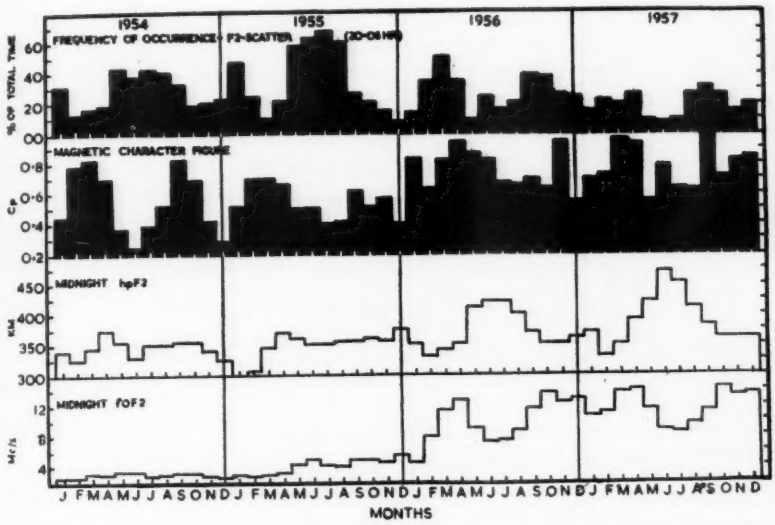

FIG. 5. Mean monthly night-time spread-F, midnight hpF_2 and midnight foF_2 at Ahmedabad together with mean International Magnetic Character Figure C_p (1954–57).

V. CORRELATION OF SPREAD-F AT DIFFERENT PLACES

For comparing the F-scatter at Ahmedabad with that at other stations, for example, Yamagawa ($\Phi = 21{\cdot}2°$ N), Delhi ($\Phi = 18{\cdot}8°$ N), Kodaikanal ($\Phi = 0{\cdot}6°$ N) and Singapore ($\Phi = 10°$ S), the months January, March, July and October 1956 were chosen. The day-to-day changes in the mean night time spread-F at the above places are shown in Figs. 6–9. The same zone times are used at all the three Indian Stations, but the time at Singapore is two hours ahead of Indian time and that at Yamagawa four hours ahead.

From the figures it is seen that

(1) In March and October, spread-F echoes are frequent in low latitudes and *there is fair to good correlation in the day-to-day occurrence of spread-F at Ahmedabad, Kodaikanal and Singapore.* Spread-F activity decreases at Delhi and becomes negligible at Yamagawa.

(2) In January and July, spread-F is less frequently observed at Ahmedabad than in the equinoxes and the agreement between the occurrences at Ahmedabad and Kodaikanal is poorer. *Even between the two equatorial stations, Kodaikanal and Singapore, the agreement is poor.* At Yamagawa on the other hand, spread-F is comparatively more frequent in January and July than in March and October, but it does not show any connection with spread-F at lower latitudes.

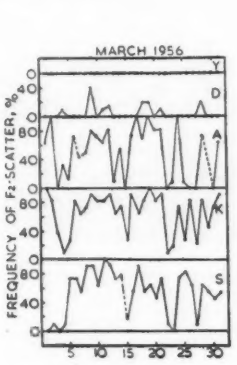

FIG. 6

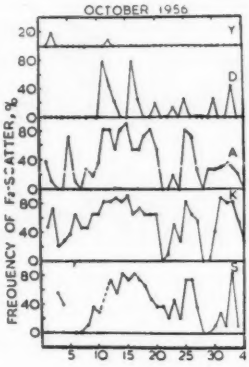

FIG. 7

FIGS. 6 and 7. Day-to-day changes of spread-F occurrence at Y = Yamagawa, D = Delhi, A = Ahmedabad, K = Kodaikanal and S = Singapore in March and October 1956.

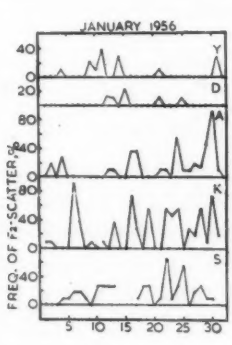

FIG. 8

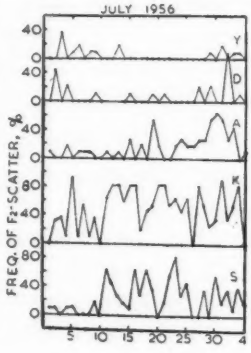

FIG. 9

FIGS. 8 and 9. Day-to-day changes of spread-F occurrence at Yamagawa, Delhi, Ahmedabad, Kodaikanal and Singapore in January and July 1956.

The above observations imply that the irregularities which cause spread-F in March and October are more widespread about the equator than in January and July. The poorer agreement of spread-F occurrences at equatorial

stations in winter and summer explains why Wright *et al.* (1956) were not able to obtain good correlation between spread-F at Ibadan and radio star scintillations at Achimota 510 km. away in solstices although both lie in the equatorial zone. From the observations of spread-F at the five places considered here, it appears that Yamagawa falls in the middle latitude zone, while Ahmedabad is very nearly in the equatorial zone in years of high sunspots.

(3) In all the months, spread-F was low on days of high magnetic activity at Indian stations and at Singapore. There is no indication of any marked change in spread-F at Yamagawa on such days. In a recent note, Lyon and others (1958) have shown that a change-over in the correlation between spread-F and C_p takes place somewhere about $\phi = 20°$ S or $I = 54°$ S in the Southern hemisphere. It appears that the change-over from low to middle latitude type of spread-F takes place somewhere near Yamagawa (geographical latitude $\phi = 31{\cdot}2$ N, magnetic dip $I = 44°$ N) in the northern hemisphere.

VI. Spread-F and F_2-Stratification

Sometimes the *h'-f* record for F_2 splits into two or more cusps or ridges at the end, or the trace may take a wavy shape with an intermediate inflection, or its ends get straightened instead of rising sharply at the critical frequency. Such changes in *h'-f* records are indicated by the letter ' H ' meaning stratification within the layer. Munro and Heisler (1953, 1956) have shown that such splitting of an *h'-f* record can take place if a travelling wave disturbance passes over a station and causes changes in the vertical distribution of ionization. Whatever may be the cause of F_2-stratification, it is found from the records so far taken at Ahmedabad that F-scatter rarely accompanies F_2-stratification. On the other hand, F-scatter generally begins subsequent to the formation of F_2-stratification. The former starts when the height falls, while the latter is observed when the height is rising.

In Fig. 10 are shown the mean diurnal variations of spread-F and F_2-stratification for 1954 and 1955. It is found that F_2-stratification has two peaks at 20 hr. and at 05–06 hr. These are also the times of temporary increases in height. On the other hand, F-scatter begins after 20 hr. and has a peak at 03 hr. It is at a falling stage at 05–06 hr. probably due to sunshine conditions.

The inverse association of F-scatter and F_2-stratification is further to be noticed from their seasonal variations. This is shown in Fig. 11. The mean percentages of F-scatter cover the period 20–06 hr. while those for F_2-stratification cover the period 19–06 hr. It is seen that F_2-stratification

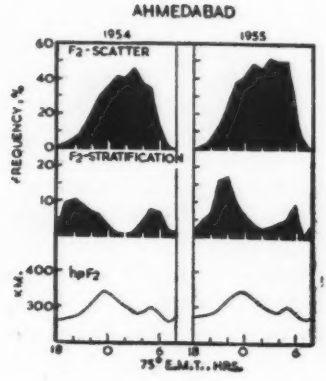

FIG. 10

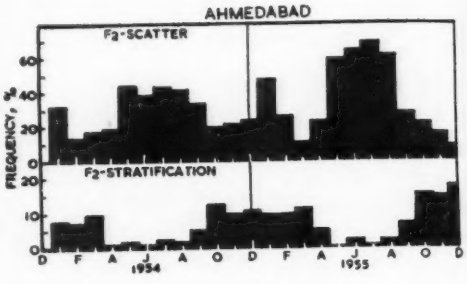

FIG. 11

FIG. 10. Comparison of mean diurnal variation of spread-F and F_2-stratification at Ahmedabad, 1954 and 1955. hpF_2 is also included for comparison.

FIG. 11. Seasonal inverse changes of spread-F and F_2-stratification at Ahmedabad 1954 and 1955.

is maximum in equinoxes, while F-scatter is minimum in these seasons. The anti-correlation between these phenomena is clear. This result is consistent with the observations of McNicol and others (1956) at Brisbane who showed that spread-F was not due to stratification in F_2.

VII. CONCLUDING REMARKS

(1) In low sunspot years, the seasonal variation of F_2-scatter has a maximum in winter at middle latitudes but maximum is summer at Ahmedabad and equatorial stations. In high sunspot years, it is still a maximum in winter in middle latitudes, but at Ahmedabad and equatorial stations, it is maximum in equinoxes instead of in summer. At latitudes higher than $\Phi = 22°$, the maximum F-scatter occurs in winter both in low as well as high sunspot years.

(2) With change in sunspot number, the maximum F-scatter occurs at or near the minimum of the sunspot cycle at Ahmedabad and equatorial stations.

(3) The time of peak occurrence of F-scatter at Ahmedabad approaches that at equatorial stations in high sunspot years.

(4) Day-to-day and monthly mean changes show that *spread-F at Ahmedabad decreases with increase in magnetic activity.*

Acknowledgements

The author is indebted to Professor K. R. Ramanathan, Director, Physical Research Laboratory, Ahmedabad, for suggesting the problem and taking keen interest in it. Thanks are also due to the Director of the Radio Research Station, Slough, the Director of the Radio Research Laboratories, Japan, the Chief Engineer, All India Radio, and the Director-General, India Meteorological Department for supplying spread-F data of the stations under them. The international Magnetic Character Figures were taken from the *Journal of Geophysical Research*.

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APPENDIX

TABLE I

Occurrence of spread-F at different places

No.	Place	Geomagnetic latitude	Time of diurnal peak Hr. LMT	Seasonal variation	Change with increase in sunspot number	Author
1	Winnipeg ..	59·5° N	03	Max. in winter	Increase	Reber from Meek (1954)
2	Slough ..	54° N	03	do.	do.	Dagg (1957)
3	Washington ..	50·3° N	03	No special season	No special preference	Reber (1954)
4	San Fransisco ..	43·6° N	03 (Winter) 00 (Summer)	Max. in winter	..	do.
5	Barton Rouge ..	41° N	Changes from 00–05 hr. from summer to winter	do.	Decrease	do.
6	Hawaii ..	20·9° N	do.	do.	Decrease to $\frac{1}{10}$ in winter and $\frac{1}{12}$ in summer	do.
7	Ahmedabad ..	13·6° N	03 (in min. s.s. years and in summer of min. s.s. years) 21–22 in winter and equinoxes of max. s.s. years	Max. in equinoxes of max. s.s. years and in summer of min. s.s. years	Decrease	Kotadia (1959)

8	Ibadan	..	10·4° N	00	Max. in local summer	..	Wright, Koster and Skinner (1956)
9	Kodaikanal	..	0·6° N	20	Max. in equinoxes	..	Bhargava (1958)
10	Huancayo	..	0·6° S	03 and 05 (Winter) 02 and 04 (Summer)	Max. in local summer	Decrease	Wells (1954)
11	Singapore	..	10° S	20	Max. in equinoxes	..	Osborne (1951)
12	Rarotonga	..	21·7° S	02–04	No special preference	No change	Reber (1954)
13	Brisbane	..	35·7° S	05 (Summer) flat over 21–05 (Winter)	Max. in winter	Decrease	Singleton (1956)
14	Watheroo	..	41·7° S	21, 00 and 05	do.	..	Reber (1954)
15	Christchurch	..	48° S	03 (Summer) 21–02 (Winter)	do.	..	do.

s.s. min. = sunspot minimum; s.s. max. = sunspot maximum.

TENSAMMETRIC STUDIES ON CORROSION INHIBITORS

Part I. Dicyclohexylamine Nitrite

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(*Central Electrochemical Research Institute, Karaikudi*)

Received May 1, 1959

(Communicated by Dr. K. S. G. Doss, F.A.SC.)

Abstract

The study of adsorption by the alternating current polarographic method is known as 'tensammetry'. This technique has been extended to the study of the adsorption characteristics of organic corrosion inhibitors with a view to elucidate the mechanism of inhibition by such compounds. The usefulness of such studies in elucidating the mechanism of inhibition by dicyclohexylamine nitrite, which is now widely used as a vapour phase corrosion inhibitor, is brought out. For this purpose, results obtained by tensammetric studies have been compared with potential measurements on the one hand and direct corrosion tests on the other and discussed.

Introduction

A large number of organic compounds are known to inhibit corrosion in aqueous media.[1–2] The mechanism of inhibition by these compounds has been studied by polarization measurements.[3] Direct measurement of the extent of adsorption of the inhibitor on the metal surface has also been attempted.[4] Direct studies on adsorption characteristics of organic corrosion inhibitors, however, involve the use of fine metal powders, the surface condition of which is generally difficult to reproduce. This difficulty may be overcome by studying the adsorption behaviour of organic compounds at the mercury surface. Among metals, mercury is unique in that it can be obtained in a highly pure chemical form and its surface characteristics are easily reproduced because of its liquid state. It is for this reason that mercury has been so widely used for the study of various metal-liquid interface phenomena including the changes in surface tension caused by capillary active substances. Electro-capillary data have been employed for the study of corrosion inhibitors.[5] Purely electrochemical methods of studying adsorption using mercury surface have also been put forward. One approach that has

been made in this direction is that of Gatos[6] based on the suppression of polarographic maximum by surface-active substances which are, otherwise, known as maxima suppressors. While this method appears to have been quite fruitful in regard to the behaviour of certain types of organic compounds having corrosion-inhibiting properties, it suffers from two important drawbacks. Firstly, the polarographic maximum is not an easily reproducible phenomenon and secondly, the mechanism of maxima suppression is not yet adequately understood. A more elegant approach to the study of adsorption of organic compounds on mercury surfaces is that of Proskurnin and Frumkin[7] and Grahame[8] who have made use of the capacity of the electrical double layer of mercury for following adsorption. They observed capacitance peaks when surface-active substances were desorbed at the metal-solution interface of a mercury electrode. The measurements were made by superposing a small low-frequency alternating voltage on to the direct potential applied to the electrode. Subsequently, Breyer and Hacobian[9] and Doss and Gupta[10] showed that the alternating current polarographic method can be used with advantage for this type of investigation. The technique consists in applying simultaneously a D.C. potential as well as a small A.C. voltage on the dropping mercury electrode of the type commonly used in polarography. The magnitude of the A.C. component of the pulsating current thus produced is a direct measure of the capacity of the electrical double layer. Percentage decrease in capacity values indicate the extent of adsorption. A new term " tensammetry " has been coined to denote studies of this kind.[25] The present paper deals with the relationship between adsorption measurements made in this manner, potential and polarization measurements and the corrosion inhibiting property of some inhibitors. The study has been particularly useful from the point of view of elucidating the mechanism of inhibition by dicyclohexylamine nitrite[11] which is widely used as a vapour phase corrosion inhibitor.[12]

Experimental

(*a*) *Compounds studied.*—(1) *p*-toluidine, (2) α-naphthylamine, (3) morpholine, (4) cyclohexylamine, (5) dicyclohexylamine, (6) dicyclohexylamine nitrite, and (7) sodium nitrite. Dicyclohexylamine nitrite is the active constituent of the trade product known as V.P.I. 260 and was obtained by recrystallisation from alcoholic solution of the trade product. The other chemicals were obtained from trade and used as such.

(*b*) *Capacity measurement.*—The method used was the same as that described in reference 10. Measurements were made in N/10 KCl solutions to which the inhibitor had been added. 0·1% solution of the inhibitor was

usually employed but where the inhibitor was not soluble to this extent as in the case of dicyclohexylamine and α-naphthylamine, a saturated solution of the inhibitor was used. Decrease in capacity was calculated by deducting the capacity (A.C. current) measured in solution containing inhibitor from that measured at the same potential in N/10 KCl solution only and this difference converted into a percentage on the original value to enable comparison. Measurements of capacity were made over a wide range of potentials on both sides of the electro-capillary zero. Decreases in capacity at different potentials are shown in Figs. 1 and 2. The capacity peaks on either side have been omitted from consideration here as the concentration of the inhibitor is not under study.

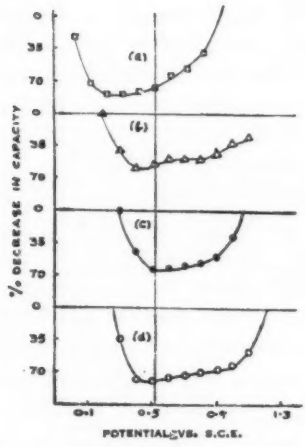

FIG. 1

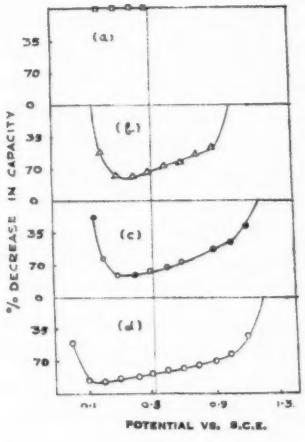

FIG. 2

FIG. 1. Percentage decrease in capacity by inhibitor at different potentials. (*a*) Cyclohexylamine. (*b*) Morpholine. (*c*) *p*-Toluidine. (*d*) α-Naphthylamine.

FIG. 2. Percentage decrease in capacity by inhibitor at different potentials. (*a*) Sodium nitrite. (*b*) Dicyclohexylamine nitrite. (*c*) Dicyclohexylamine neutralised to pH 7. (*d*) Dicyclohexylamine.

(*c*) *Potential and polarization measurements.*—The potentials were measured by the Poggendorf method using a Beckman pH meter as the zero reading instrument. This made it possible to make potential measurements without passage of more than 10^{-11} amperes on off balance. Polarization measurements were carried out by external application of current with a duplicate specimen as the auxiliary electrode. The procedure followed in the preparation of steel specimens for potential and polarization measurements was similar to that described by Brasher.[13] All measurements were

made at $35 \pm 0{\cdot}1°$ C. The finish given to these specimens is similar to that given in the case of specimens used in corrosion test.

(*d*) *Corrosion tests.*—3″×2″ mild steel specimens were cut, uniformly abraded with 0 emery, degreased with methanol, benzene and acetone and used. The electrolyte used for the corrosion tests was 0·001% NaCl with and without inhibitor. The solution was aerated before test. The experiments were carried out in triplicate and the specimens were suspended in the electrolyte with the help of glass hooks such that the top edge of the specimens was more than 1″ below the water line.

Results

(*a*) *Changes in capacity.*—The percentage decrease in capacity at various potentials on both sides of the electro-capillary zero of the various inhibitors studied are given in Figs. 1 and 2. In the case of dicyclohexylamine the values were also determined after neutralizing the solution to pH 7 with dilute sulphuric acid solution to enable comparison with dicyclohexylamine nitrite which in its pure form gives a neutral solution. It may be seen from the two figures that (i) all the compounds studied excepting sodium nitrite show adsorption on mercury surface, (ii) the adsorption is on both sides of the electro-capillary zero, (iii) the extent of adsorption at different potentials varies from inhibitor to inhibitor, (iv) α-naphthylamine and *p*-toluidine show adsorption preferentially on the negative side of the electro-capillary zero, (v) morpholine, cyclohexylamine and dicyclohexylamine are adsorbed to the maximum extent at the electro-capillary zero, and the adsorption on both sides extends over a wide range, (vi) the range of potentials over which adsorption takes place and the extent of adsorption is highest in the case of dicyclohexylamine and least in the case of morpholine, (vii) this adsorption decreases at the lower pH and, lastly (viii) the adsorption characteristics of dicyclohexylamine nitrite and dicyclohexylamine at pH 7 (*i.e.*, when the dicyclohexylamine has been converted into sulphate) are very similar to each other.

(*b*) *Potential and polarization measurements.*—Steady potentials of mild steel specimens in 0·001% NaCl solutions containing the inhibitors are given in Table I. It may be seen from Table I that changes in potential in the nobler direction, which usually indicates passivation of the metal surface, are observed only in the case of sodium nitrite, dicyclohexylamine nitrite, cyclohexylamine and morpholine. No such shift is observed in the case of the other chemicals.

Coming to anodic and cathodic polarization measurements at different current densities given in Figs. 3 and 4, one finds that the results closely

TABLE I

Potentials of mild steel specimens in 0·001% NaCl solution containing organic chemical at the end of 3 hours of immersion

Sl. No.	System	Potential *vs.* saturated calomel electrode
1	Without inhibitor ..	− 0·66
2	Solution saturated with α-naphthylamine	− 0·53
3	0–1% *p*-Toluidine ..	− 0·67
4	Solution saturated with dicyclohexylamine	− 0·60
5	0·1% Morpholine ..	− 0·32
6	0·1% Cyclohexylamine ..	− 0·13
7	0·1% Sodium nitrite ..	− 0·02
8	0·1% Dicyclohexylamine nitrite ..	+ 0·02

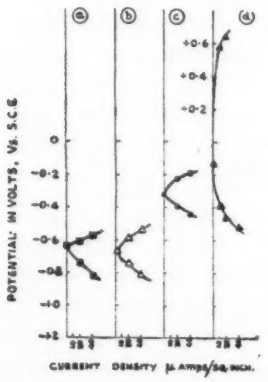

FIG. 3

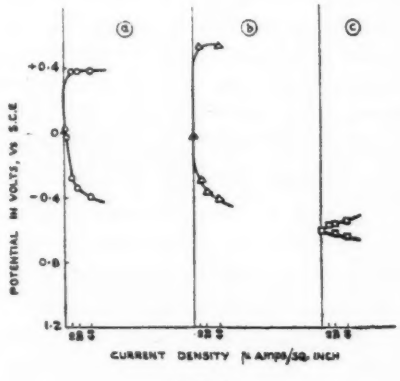

FIG. 4

FIG. 3. Potential current density curves in 0·001% NaCl solution. (*a*) No inhibitor. (*b*) *p*-Toluidine. (*c*) Morpholine. (*d*) Cyclohexylamine.

FIG. 4. Potential current density curves in 0·001% NaCl solution. (*a*) Dicyclohexylamine nitrite. (*b*) Sodium nitrite. (*c*) Dicyclohexylamine.

paralleled potential data and corrosion data given in the next section. The only chemicals which bring about increased polarization of the steel specimens are sodium nitrite, dicyclohexylamine nitrite, cyclohexylamine and morpholine. The extent of polarization follows the same order as corrosion inhibition data. Both sodium nitrite and dicyclohexylamine nitrite polarise to the same extent, cyclohexylamine to a lesser extent and morpholine to a still lesser extent.

(*c*) *Corrosion inhibition data.*—The period for which complete protection is given by the different inhibitors in the corroding medium, and loss in weight at the end of 15 days of test are given in Table II.

TABLE II

Data on corrosion inhibition

Sl. No.	System	Period for which complete protection is obtained
1	Without inhibitor	.. < One hour
2	α-Naphthylamine	.. < One hour
3	*p*-Toluidine	.. < One hour
4	Morpholine	.. Two days
5	Cyclohexylamine	.. Three days
6	Dicyclohexylamine	.. < One hour
7	Dicyclohexylamine nitrite	.. > One month
8	Sodium nitrite	.. > One month

It is seen from Table II that practically no inhibition is given by *p*-toluidine, α-naphthylamine and dicyclohexylamine, in neutral solution containing chloride. Morpholine gives protection for a short duration but once rusting commences at the glass-metal contact, it spreads quite rapidly to the rest of the metal surface. Cyclohexylamine gives considerable inhibition and localizes rusting even when it has commenced. Sodium nitrite and dicyclohexylamine nitrite both containing nitrite ion give complete inhibition during the entire duration of test.

DISCUSSION

Corrosion is retarded by the presence of a barrier between the metallic material and the environment and this barrier may be produced either by a protective oxide film formed at the metal surface or by adsorbed particles. The adsorption of gelatine on mild steel has been demonstrated by Rhodes and Kuhn[14] in terms of the rate of hydrogen evolution from acid solution. Very similar inhibition is given by all types of amines and N-ring bodies. It has been suggested by Warner[15] that amines are preferentially adsorbed at those points of the metal surface that are in its absence the most active for the cathodic discharge of hydrogen ions. The increase of hydrogen over potential produced by such substances at cathodes operating at much more negative potentials than those found in acid corrosion has been brought forward as evidence in support of this theory.[16–18] But it is now known that very similar inhibition is produced by many other kinds of molecules, some of which can scarcely be supposed to accept protons even in the most acid solution. Machu,[19] therefore, suggested general adsorption as the cause of inhibition by organic compounds which did not react with the metal surface. Hoar[20] has pointed out that a mainly cathodic inhibitor acting merely by blocking cathodic sites must lead to a shift of the compromise or corrosion potential in the negative direction and conversely a mainly anodic inhibitor must lead to ennoblement of potential in accordance with the Evan's diagram. This has also lead Hoar[21] to conclude that N-inhibitors including quinolines and substituted quinolines are readily adsorbed on the anodic than on the cathodic sites. Antropov[22] has drawn pointed attention to his concept of ψ potential of metals based on electro-capillary zero. According to him, adsorption is governed by the intrinsic charge of the metal surface and not in terms of the local cell theory of corrosion and the presence of anodic and cathodic sites on the metal surface. Depending upon the corrosion potential of a metal as given by the hydrogen scale both anodic and cathodic areas of the metal surface will be negatively or positively charged, or both negatively and positively charged. He has, therefore, suggested a new scale of potential known as ψ potential obtained by the difference between the electro-capillary zero potential and the potential on the hydrogen scale. That this approach is considered more fundamental from the point of view of the study of adsorption has already been pointed out in the Introduction to this paper. The results obtained in this paper may also be satisfactorily understood in terms of this approach. The potential at the electro-capillary maximum of steel has been shown to be very near that of mercury. Steel in neutral chloride solution has an initial potential of $-0{\cdot}45$ volts against saturated calomel electrode which quickly falls to a potential of $-0{\cdot}65$ volts.

At the initial potential part of the surface may be expected to be slightly positively charged.[22a] Substances which are adsorbed on the positive side of the capacity curve are likely to give more inhibition under these conditions than those showing adsorption at the negative side. Of the different chemicals studied, it is seen that only morpholine, cyclohexylamine and dicyclohexylamine show pronounced adsorption on the positive side of the electrocapillary zero. Two of these chemicals cyclohexylamine and morpholine give inhibition to some degree; cyclohexylamine shows more adsorption and also shows more inhibition. The behaviour of dicyclohexylamine is not clear. In this case, as in the case of a large number of surface-active substances, adsorption has not been followed by corrosion inhibition. In the case of dicyclohexylamine nitrite, the observed corrosion inhibition may be attributed to the combined effect of adsorption of inhibitor as well as the property of the nitrite ion to form a protective oxide film of metal surface. The inability of α-naphthylamine and *p*-toluidine to give inhibition in neutral solution may also be explained on this basis. They show adsorption mainly on the negative side of the electro-capillary zero and this adsorption is favoured in acid solutions in which the corrosion potential of steel is more negative and the steel surface is also negatively charged.

It may also be noticed that such adsorption as those considered above shift the potential of the metal. When the potential is shifted in the nobler direction (adsorption of compounds like cyclohexylamine and morpholine) is further favoured that is why these chemicals which cause considerable changes in potential in the nobler direction are also the only amines among those considered which show inhibition to an appreciable extent in neutral solution. The same is observed in the case of dicyclohexylamine nitrite where adsorption enables the inhibitor being brought very near to the metal surface. However, the situation here is complicated by the existence of the nitrite group which really brings about the observed corrosion inhibition in the same way as sodium nitrite which by itself does not show any adsorption. The mechanism of inhibition by nitrite ion has been dealt with by other workers[23–24] and it has been shown to form a protective oxide film on the metal surface.

Conclusion

The usefulness of adsorption studies by tensammetric measurements with corrosion inhibitors has been brought out. It has been shown that dicyclohexylamine nitrite gives corrosion prevention in neutral media both by the inhibitive action of the nitrite ion on the one hand and the property of adsorption displayed by dicyclohexylamine group on the other.

ACKNOWLEDGEMENT

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THE STOBBE CONDENSATION OF ANISALDEHYDE AND DIMETHYL SUCCINATE

Synthesis of the Lactone of 2-Carboxy-4-Hydroxy-6-Methoxytetralone-1*

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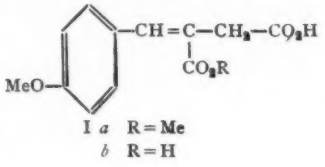
THE Stobbe condensation between *p*-methoxybenzaldehyde and diethyl succinate had been reported to yield only the dialkylidenesuccinic acid,[1] but Campbell, Cella and Campbell[2] adopting the procedure of Cornforth, Hughes and Lions[3] have obtained *p*-methoxyphenylitaconic acid. During the course of a scheme of work, we obtained methyl hydrogen *p*-methoxyphenylitaconate (I *a*) by condensing *p*-methoxybenzaldehyde with dimethyl succinate in the presence of potassium *tert.*-butoxide; and in view of the recent publication of El-Abbady and El-Assal[4] we are reporting our experiments.

The unsaturated half ester (I *a*) on reduction with 10% palladium on carbon yielded methyl hydrogen α-*p*-methoxybenzylsuccinate (II *a*) which on cyclisation with polyphosphoric acid gave a mixture of the tetralone compounds (IV *a* and IV *b*), the acid (IV *b*) being evidently formed by hydrolysis of the ester (IV *a*). The structures of these were proved by comparison with authentic specimens.[2]



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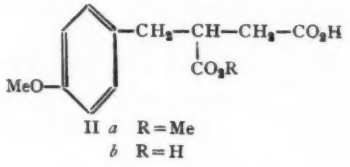

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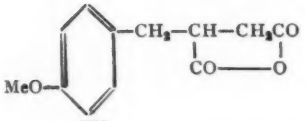

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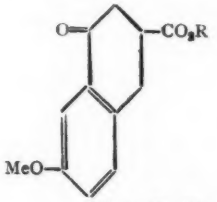

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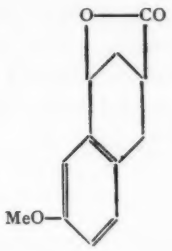
* Presented at the Forty-fifth Session of the Indian Science Congress held at Madras in 1958.



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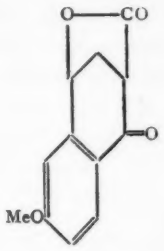

VI

However, it was found that 3-carboxy-7-methoxytetralone-1 (IV *b*) could be most conveniently prepared by condensing *p*-methoxybenzaldehyde and dimethyl succinate in methanolic sodium methoxide,[3] followed by reduction of an alkaline solution of the *p*-methoxyphenylitaconic acid (I *b*) with nickel-aluminium alloy[5 a,b] when the saturated acid (II *b*) was obtained (there being no loss of the methoxyl group[5 c]) in 95% yield. The anhydride of the diacid (II *b*) was cyclised with anhydrous aluminium chloride in nitrobenzene to give 3-carboxy-7-methoxytetralone-1 (IV *b*) in 70% yield.

An aqueous solution of the sodium salt of 3-carboxy-7-methoxytetralone-1 on reduction with sodium borohydride followed by lactonisation of the hydroxy acid gave a poor yield of the lactone (V). 3-Methoxycarbonyl-7-methoxytetralone-1 (IV *a*) on reduction with aluminium isopropoxide gave in the neutral fraction the lactone (V) as one of the products. Oxidation of this lactone (V) with chromium trioxide in acetic acid yielded the lactone of 2-carboxy-4-hydroxy-6-methoxytetralone-1 (VI).

Experimental

Stobbe Condensation of p-*Methoxybenzaldehyde and Dimethyl Succinate*

(*a*) *With Potassium* tert.-*butoxide*.—To a stirred solution of potassium *tert*.-butoxide, from potassium (10·80 g.) and *tert*.-butanol (270 ml.), under nitrogen was added dimethyl succinate (73·4 g.) which was washed down with *tert*.-butanol (15 ml.). To this was added with vigorous stirring during 1·5 hour freshly distilled *p*-methoxybenzaldehyde (32·64 g.) in *tert*.-butanol (30 ml.). After stirring for 10 hr. at room temperature (*ca*. 23°) it was cooled and dilute hydrochloric acid (25·3 ml. of conc. hydrochloric acid in 168 ml. of water) was added gradually with stirring. Most of the butanol was distilled off under reduced pressure, the residue was taken up in ether, and the ethereal solution extracted with saturated sodium bicarbonate solution at 0°. The alkaline solution was run into an excess of cold hydrochloric acid, and the acid solution extracted with ether, the ethereal phase was washed

with cold water, and dried, and the ether was distilled off. On cooling, a solid (59·3 g.) melting at 87–96 ° was obtained. After two crystallisations from benzene-light petroleum (40–60°) *methyl hydrogen* p-*methoxyphenylitaconate* (I *a*) (35·7 g.; m.p. 118–19°, lit.[4] 119–20°; U.V.: $\lambda_{max.}^{alc.}$ 294 mμ log ε 4·42) was obtained (Found: C, 62·58; H, 5·52. $C_{13}H_{14}O_5$ requires C, 62·40; H, 5·64%. Equivalent weight: Found, 249·4; $C_{13}H_{14}O_5$ requires 250·2).

(*b*) *With sodium methoxide.*[3]—To a stirred solution of methanolic sodium methoxide, from sodium (57·5 g.) and methanol (450 ml.), was gradually added under reflux a mixture of *p*-methoxybenzaldehyde (136 g.) and dimethylsuccinate (160 g.) over a period of 0·5 hr. The stirred yellow reaction mixture was refluxed for 2·5 hr. and then water (500 ml.) was added cautiously with simultaneous distillation of methanol. When methanol had ceased to distil, the reaction mixture was diluted with a further 750 ml. of water, extracted twice with ether (300 ml.) and then the alkaline phase was slowly run in with stirring to an excess of ice-cold hydrochloric acid. The precipitated acid on repeated crystallisations from aqueous ethanol yielded *p*-methoxyphenylitaconic acid (I *b*) (172 g.; m.p. 192–94°, recorded 188–91°,[2] 202–03°[4]; U.V.: $\lambda_{max.}^{alc.}$ 294 mμ log ε 4·36).

Methyl hydrogen α-p-*methoxybenzylsuccinate* (*II* a).—The unsaturated half-ester (I *a*) (2·1 g.) in dioxane (30 ml.) containing 60% perchloric acid (1 ml.) was hydrogenated at room temperature over 10% palladium on carbon. After filtering off the catalyst, the reduced material was taken up in a large quantity of ether and repeatedly washed with ice-cold water till the aqueous phase was free of acid. On drying the ethereal phase and on complete removal of the solvent *methyl hydrogen* α-*p-methoxybenzylsuccinate* (II *a*) (1·91 g.; U.V.: $\lambda_{max.}^{alc.}$ 226 mμ log ε 4·06, 277·5 mμ log ε 3·25) was obtained as a semi-solid. A sample was purified by molecular distillation for analysis (Found: C, 61·75; H, 6·34. $C_{13}H_{16}O_5$ requires C, 61·87; H, 6·35%).

p-*Methoxybenzylsuccinic acid* (*II* b).—*p*-Methoxyphenylitaconic acid (I *b*) (42·5 g.) was dissolved in 1 l. of 12% aqueous sodium hydroxide. A few drops of octyl alcohol was introduced and then to the stirred solution at 90° was gradually added 1 : 1-nickel-aluminium alloy (85 g.) over 1·75 hr. After stirring for a further 0·75 hr. at 90°, the hot solution was cautiously filtered under suction[5a] and the catalyst washed well with water. The warm alkaline solution was then added slowly with stirring to a large excess of hydrochloric acid. The reduced acid was either filtered (if solid), or extracted with ether (if oily) and the solvent removed, when *p*-methoxy-

benzylsuccinic acid (42·0 g.; m.p. 95–98° or 106–09°) was obtained. Recrystallisation from dilute alcohol or dilute acetic acid yielded either of the polymorphs m.p. 101° or 114° showing no depression with samples prepared by the procedure of Campbell *et al.*[2]

Cyclisation of Methyl Hydrogen α-p-*Methoxybenzylsuccinate* (*II* a)

(*a*) *With polyphosphoric acid.*—To a stirred solution of phosphorous pentoxide (30 g.) in syrupy phosphoric acid (sp. gr. 1·75; 15 ml.) was added the half-ester (II *a*) (4·9 g.) under anhydrous conditions. It was heated for 40 min. on a steam-bath, and then to the reaction mixture was added crushed ice (100 g.) and water (100 ml.). It was extracted with ether (there was a considerable quantity of tar formed), and the ethereal solution washed with ice-cold 5% alkali, then with brine and dried. On removal of the solvent, the neutral phase deposited 3-methoxycarbonyl-7-methoxytetralone-1 (IV *a*) (0·6 g.). On crystallisation from ether-light petroleum (40–60°) the ester melted at 80–81° (recorded 78–79·5°[2]); U.V.: $\lambda_{max.}^{alc.}$ 253 mμ log ε 3·98, 323 mμ log ε 3·19 (Found: C, 67·08; H, 6·09. $C_{13}H_{14}O_4$ requires C, 66·65; H, 6·02%).

The alkaline wash on running into ice-cold hydrochloric acid yielded 3-carboxy-7-methoxytetralone-1 (IV *b*) (1·8 g.). After crystallisation from acetone-benzene it melted at 152–53° (recorded 149–51°[2]); U.V.: $\lambda_{max.}^{alc.}$ 253 mμ log ε 3·99, 322 mμ log ε 3·21 (Found: C, 65·65; H, 5·35. $C_{12}H_{12}O_4$ requires C, 65·46; H, 5·50%).

(*b*) *With aluminium chloride.*—To a suspension of the half-ester (II *a*) (7·15 g.) in dry benzene (100 ml.) was added dropwise a solution of thionyl chloride (5 ml.) in dry benzene (15 ml.) with swirling. After refluxing gently for 2·75 hr. the excess thionyl chloride and all the benzene were removed completely under suction. To a stirred solution of the crude acid chloride in benzene (100 ml.) kept at 0° was added a solution of aluminium chloride (9·5 g.) in dry benzene (20 ml.). After leaving it overnight at room temperature, it was decomposed with ice-cold 2 N-hydrochloric acid, and extracted with ether. After removal of the solvent the crude oily material was dried thoroughly and saponified with 10% aqueous potassium hydroxide. On working up, 3-carboxy-7-methoxytetralone-1 (IV *b*) (1·2 g.; m.p. 151–52°) was obtained.

3-*Carboxy-7-methoxytetralone*-1 (*IV* b) *from* p-*methoxybenzylsuccinic acid* (*II* b).—*p*-Methoxybenzylsuccinic acid (72·3 g.) was converted to the anhydride (III) by treatment with an excess of acetyl chloride at room temperature for 6 hours. (A sample crystallised from benzene-hexane melted at 91–92°, lit.[3] 90–92°.) A suspension of the crude anhydride (64·8 g.; m.p.

87–90°) in nitrobenzene (150 ml.) was added portionwise over a period of 20 mins. at room temperature to a vigorously stirred solution of aluminium chloride (125 g.) in nitrobenzene (400 ml.); the temperature rose to about 40°. It was left overnight (15 hr.) with stirring under anhydrous conditions. The reaction mixture was decomposed with ice and hydrochloric acid and the nitrobenzene removed by steam-distillation. The solid product on repeated crystallisations from hot water (charcoal) yielded 3-carboxy-7-methoxytetralone-1 (IV *b*) (46·2 g.; yield 71%; m.p. 151–53°).

To an ethereal suspension of 3-carboxy-7-methoxytetralone-1 (IV *b*) (2·0 g.) kept at 0°, was added a solution of diazomethane (from 3·0 g. of nitrosomethylurea) in ether in small portions. The resulting pale yellow solution after standing for 5 min., was treated with a little acetic acid and then washed with ice-cold potassium carbonate solution and water. After drying, on removal of the solvent, the residue (2·1 g.) melted at 70–75° which on crystallisation from ether-light petroleum (40–60°) furnished 3-methoxycarbonyl-7-methoxytetralone-1 (IV *a*), m.p. 80°.

Lactone of 1-*Hydroxy*-3-*carboxy*-7-*methoxytetralin* (*V*)

(*a*) *Reduction with sodium borohydride.*—To a solution of 3-carboxy-7-methoxytetralone-1 (IV *b*) (5·0 g.) in 1 N-sodium hydroxide (22·8 ml.) was added sodium borohydride (0·65 g.) with swirling at room temperature. The reaction mixture after standing overnight was cooled and acidified with dilute sulphuric acid (6·5 ml. of conc. acid in 125 ml. water). It was then warmed for 15 min. on a steam-bath, cooled and extracted with ether. The ethereal solution was washed with sodium bicarbonate solution, water and dried. On removal of the ether, a solid residue (1·9 g.; m.p. 101°) was obtained. Crystallisation from benzene-hexane yielded the *lactone of* 1-*hydroxy*-3-*carboxy*-7-*methoxytetralin* (1·8 g.); m.p. 103°; U.V.: $\lambda_{max.}^{alc.}$ 232 mμ log ε 4·00, 280 mμ log ε 3·36; I.R.: 1792 cm.$^{-1}$ (γ-lactone) (Found: C, 70·31; H, 6·01. $C_{12}H_{12}O_3$ requires C, 70·58, H, 5·93%).

(*b*) *Reduction with aluminium isopropoxide.*—From 3-methoxycarbonyl-7-methoxytetralone-1 (IV *a*) (2·32 g.), aluminium isopropoxide (2·1 g.) and dry isopropanol (30 ml.), acetone was distilled off using a Hahn condenser containing methanol under anhydrous conditions. After complete removal of the acetone much of the isopropanol was removed under suction and the residue was decomposed at 0° with ice-cold hydrochloric acid (3·5 ml. conc. acid and 17·5 ml. water). The product was extracted with ether and the ethereal solution was washed with ice-cold sodium bicarbonate solution, brine and dried (Na_2SO_4). Most of the ether was removed and light petroleum (40–60°) was added to it, and then the material was left in the

refrigerator. The precipitated solid was filtered and washed with a little dry ether (yield 0·09 g.; m.p. 102–03°). The lactone was recrystallised from ether-light petroleum (40–60°), m.p. 103°.

Lactone of 2-*carboxy*-4-*hydroxy*-6-*methoxytetralone*-1 (*VI*).—To a solution of the lactone of 1-hydroxy-3-carboxy-7-methoxytetralin (V) (0·2 g.) in acetic acid (2·1 ml.) and propionic acid (0·4 ml.) at 0° was added with swirling, in the course of 8 min., a solution of chromium trioxide (0·2 g.) in water (0·2 ml.) and acetic acid (1·1 ml.). After keeping at 0° for a further 40 min. it was left at room temperature for 24 hr. After addition of a small quantity of methanol, the deep violet product was poured into water (50 ml.) and extracted with ether. The combined ether extract was washed with ice-cold potassium carbonate solution, water and dried. On distillation of the ether a white precipitate was obtained (0·14 g.; m.p. 134–36°). *The lactone of* 2-*carboxy*-4-*hydroxy*-6-*methoxytetralone*-1 (VI) was recrystallised from ether-light petroleum (40–60°), m.p. 136°; U.V.: $\lambda_{max}^{alc.}$ 228 mμ log ϵ 4·31, 292·5 mμ log ϵ 4·31; I.R.: 1790 cm.$^{-1}$ (γ-lactone), 1700 cm.$^{-1}$ (aryl conjugated carbonyl) (Found: C, 65·72; H, 4·57. $C_{12}H_{10}O_4$ requires C, 66·04; H, 4·62%).

Summary

Condensation of anisaldehyde and dimethyl succinate in presence of potassium *tert.*-butoxide yielded methyl hydrogen *p*-methoxyphenylitaconate. Reduction followed by cyclisation with polyphosphoric acid furnished 3-methoxycarbonyl-7-methoxytetralone-1 and 3-carboxy-7-methoxytetralone-1. The lactone of 1-hydroxy-3-carboxy-7-methoxy-tetralin was obtained as a product in the aluminium isopropoxide reduction of 3-methoxycarbonyl-7-methoxytetralone-1; or by reducing the sodium salt of 3-carboxy-7-methoxytetralone-1 with sodium borohydride followed by lactonisation with dilute sulphuric acid. Oxidation of this lactone yielded the lactone of 2-carboxy-4-hydroxy-6-methoxytetralone-1.

Acknowledgements

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ERRATA

Vol. L, No. 3

Page		*For*	*Read*
169	3rd line from bottom	$(\alpha)_D^{28}$	$[\alpha]_D^{28}$
173	Last line above Summary	$C_9H_{15}O_3$ requires: C, 63·1; H, 8·8%	$C_9H_{16}O_3$ requires: C, 62·8; H, 9·4%

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